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REMOVING ORGANICS FROM
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BY COMBINED OZONATION AND ADSORPTION

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16. ABSTRACT

This project was conducted on both a pilot and laboratory scale to understand the effects of ozonation and the relationship between adsorption and biological activity during water treatment with ozone and granular activated carbon. The removal of trace organic substances of health concern at the ng/L to ug/L level and the removal of Total Organic Carbon at the mg/L level were carefully monitored along with microbial parameters of biological speciation and growth rate. This report summarizes the results of chemical (inorganic and organic) and microbiological analyses and evaluates the performance of pilot plant schemes for granular activated treatment at Philadelphia. It provides a detailed analysis of the unit operations of ozonation and granular activated carbon treatment when used in combinations of O_3/GAC, O_3/SAND, Cl_2/GAC, Cl_2+O_3/GAC and no-disinfection/GAC following the conventional treatment processes of raw water settling, coagulation, flocculation, sedimentation, and rapid sand filtration. System comparisons were made using estimated total costs of each unit process, as determined by the carbon reactivation rate needed to maintain various effluent criteria.

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FOREWORD

The U.S. Environmental Protection Agency was created because of increasing public and government concern about the dangers of pollution to the health and welfare of the American people. Noxious air, foul water, and spoiled land are tragic testimonies to the deterioration of our natural environment. The complexity of that environment and the interplay of its components require a concentrated and integrated attack on the problem.

Research and development is that necessary first step in problem solution, and it involves defining the problem, measuring its impact, and searching for solutions. The Municipal Environmental Research Laboratory develops new and improved technology and systems to prevent, treat, and manage wastewater and solid and hazardous waste pollutant discharges from municipal and community sources, to preserve and treat public drinking water supplies, and to minimize the adverse economic, social, health, and aesthetic effects of pollution. This publication is one of the products of that research and is a most vital communications link between the researcher and the user community.

Carbon adsorption is one method of removing compounds of potential health concern from drinking water. The technical and economic aspects of its use (both with and without preozonation) is investigated in this report.

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Director
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ABSTRACT

Laboratory and pilot plant studies were conducted to investigate the combined unit processes of oxidation by ozonation and adsorption by granular activated carbon (GAC). In addition, the effect of chlorine and chlorine by-products on the ozone and GAC processes was investigated.

The study used Delaware River water that was treated by two coagulation/filtration plants: a full-scale plant operating with a 2 mg/l free chlorine residual and a 30,000 gpd pilot plant operating without any disinfection. The rapid sand filter effluents from each were applied to parallel GAC and O_3/GAC systems. The GAC beds remained in service between 360 and 500 days.

The removal of trace organic substances at the ng/l to ug/l level and the removal of TOC at the mg/l level were carefully monitored along with microbial parameters of biological speciation and growth rates. System comparisons were made using estimated total costs of each unit process, as determined by the carbon regeneration rate needed to maintain various effluent criteria.

This report was submitted in fulfillment of cooperative agreement No. 806256-02 by The City of Philadelphia Water Department under the sponsorship of the U.S. Environmental Protection Agency. This report covers the period 4/1/80 to 11/30/81, and work was completed as of 8/31/82.

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LIST OF ABBREVIATIONS

A254	ultraviolet absorbance at 254 nm
AFAH	aerobic and facultative anaerobic heterotrophic
AWT	advanced water treatment
BAC	biologically activated carbon
BD	below detectable limits
BOD	biological oxygen demand
BROMO	bromoform
CCI	construction cost index
cfu	colony forming units
CHLO	chloroform
CLAR	clarifier
COD	chemical oxygen demand
CON	control system
DBCM	dibromochloromethane
DCBM	dichlorobromomethane
DCE	dichloroethane
DCP	dichloropropane
DMM	dimethoxymethane
DO	dissolved oxygen
DOC	dissolved organic carbon
EBCT	empty bed contact time
EXP	experimental system
G:L	gas to liquid ratio
GAC	granular activated carbon
GC	gas chromatogram
GPD	gallons per day
GPM	gallons per minute
IDS	indigo disulfonate
KD	Kuderna-Danish flask
KI	Kovats Index
MAC	maximum adsorption capacity
MCL	maximum contaminant level
MEK	methyl ethyl ketone
MG	million gallons
MGD	million gallons per day
MPC	modified plate count
MQL	minimum quantifiable Limits
MRR	macroreticular resin
MT	multi-tap GAC system
mw	molecular weight
NR	no regeneration
O_3	ozone
O_3C	ozone contactor
O & M	operation & maintenance
O_3RT	ozone retention tank
OU	ozone utilized
PAC	powdered activated carbon
PP	pilot plant
ppb	parts per billion
ppm	parts per million
PWD	Phila.Water Department
RRT	relative retention time
RSF	rapid sand filter
RWB	raw water basin
SCFH	standard cubic feet per hour
SCFM	standard cubic feet per minute
SD	standard deviation
SEA	soil extract agar
SEM	scanning electron microscopy
SPC	standard plate count
THM	trihalomethane
THMFP	trihalomethane formation potential
THMT	terminal trihalomethane
TOC	total organic carbon
TOX	total organic halogens
UV	ultraviolet absorbance @ 254 nm

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SECTION 1

INTRODUCTION

The removal of trace organic substances of health concern from drinking water by adsorption onto granular activated carbon (GAC) has been repeatedly demonstrated during research studies at Philadelphia (1). Though GAC systems have been shown to be both technically feasible and operationally manageable, they can place a severe economic burden on water utilities because of the substantial operating and maintenance costs associated with frequent carbon regeneration. The regeneration of carbon, needed to maintain the integrity of the adsorption process, may account for up to 75% of the operating and maintenance costs (based on a 3-month regeneration frequency (2)). Thus the primary concern for the practical use of GAC is lowering operating costs by increasing the useful life of GAC for the removal of trace organic compounds of potential health concern.

Trace organic compounds that pose a potential health threat are only a small portion of the organic compounds present, representing about 10% of the total organic carbon (TOC) (3). Though the high-molecular-weight organic compounds found in drinking water (which account for the remaining 90% of the TOC) are not of direct human health concern, some are precursors to potential carcinogens (e.g., $CHCl_3$), and others may compete with more harmful organics for the limited adsorption sites available on the carbon.

To reduce the load of naturally occurring TOC and limit the presence of possibly harmful organics that can arise from chlorination of natural water (e.g. trihalomethanes), a pilot study was completed using combinations of ozonation and GAC or sand and comparing these operations to combinations of chlorination, chlorination/ozonation, and GAC.

Through the preozonation of the water, some of the higher-molecular-weight humic substances (such as humic and fulvic acids and aromatic compounds) can be oxidized into more biodegradable forms (4). These lower-molecular-weight organic compounds are then potentially available as a food source for microbes on the GAC bed. Preozonation may thus result in the availability of more adsorptive sites for the less biodegradable, more harmful organic compounds that are poorly oxidized (e.g. chloroform and 1,2-dichloropropane). European experience with this type of treatment process has been extensively reviewed by Rice et al. (5) and has been collectively called the biologically enhanced granular activated carbon (BEGAC) process, or more simply, the biologically activated carbon (BAC) process.

TABLE 1. HEALTH EFFECT PRIORITIES FOR CHEMICAL PARAMETERS (1)

Group I -	CARCINOGENS AND SUSPECTED CARCINOGENS listed by (1) National Academy of Science (3,9) (2) National Cancer Institute (10)
Group IA -	MUTAGENS, TERATOGENS AND PROMOTORS listed by (1) National Cancer Institute (10)
Group II -	PRIORITY POLLUTANTS listed in (1) NRDC *v* Train (11)
Group III-	OTHER COMPOUNDS OF POTENTIAL HEALTH EFFECT listed by (1) National Academy of Science (9)
Group IV -	PRECURSORS that react with a disinfectant to produce a by-product which falls into Groups I - III.
Group V -	HUMIC SUBSTANCES AND NON-HEALTH EFFECT COMPOUNDS IN HIGH CONCENTRATION which can compete with compounds of Groups I - III and cause earlier breakthrough of these compounds on GAC columns.

The present project was conducted on both a pilot and laboratory scale to understand the effects of ozonation and the relationship between adsorption and biological activity during water treatment with ozone and GAC. The removal of trace organic substances of health concern at the ng/l to ug/l level and the removal of TOC at the mg/l level were carefully monitored along with microbial parameters of biological speciation and growth rates. The frame of reference for this study has been previously described (Figure 1) as design elements for the carbon adsorption process (1). The engineering evaluation and economic analysis derived from the biological and chemical considerations of nonspecific, specific, and screening protocols are evaluated in terms of health effect priorities (Table 1).

Table 1 shows the chemical groups considered for design of GAC systems. The primary aim for design would be to assure removal of chemicals of *known* health concern (e.g., Group I compounds). Maximum contaminant levels (MCL's) have already been proposed or established for certain Group I compounds, e.g. haloforms, pesticides, 13 chlorinated volatiles, and benzene (6-8). A well designed adsorption process must be flexible enough to accommodate the removal of other Group I compounds to protect the public health. When other MCL's are developed, Group I compounds are expected to be primary targets.

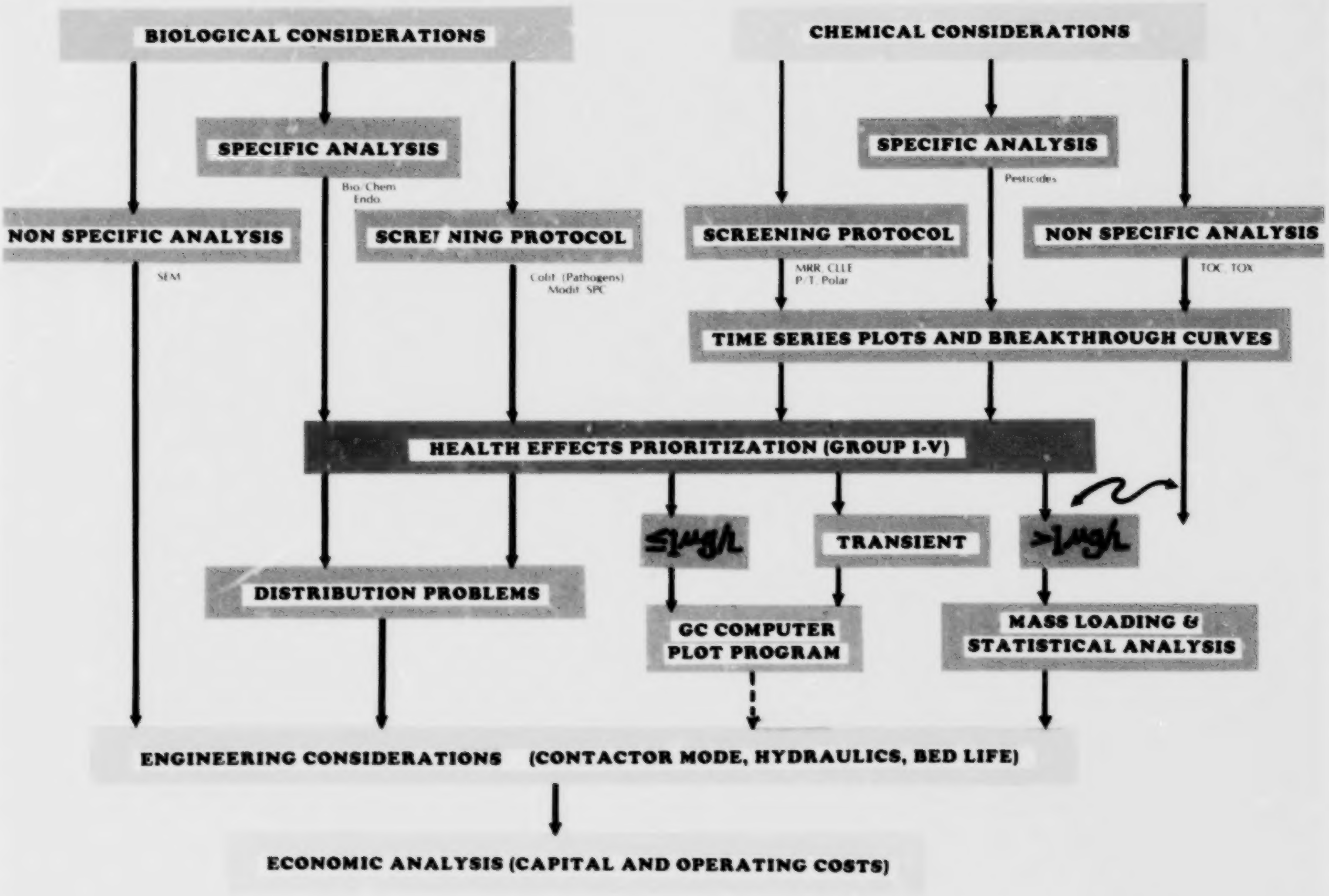

BIOLOGICAL CONSIDERATIONS
CHEMICAL CONSIDERATIONS
SPECIFIC ANALYSIS
Bio/Chem
Endo.
SPECIFIC ANALYSIS
Pesticides
NON SPECIFIC ANALYSIS
SEM
SCREENING PROTOCOL
Colif (Pathogens)
Modif. SPC
SCREENING PROTOCOL
MRR, CLLE
P/T, Polar
NON SPECIFIC ANALYSIS
TOC, TOX
TIME SERIES PLOTS AND BREAKTHROUGH CURVES
HEALTH EFFECTS PRIORITIZATION (GROUP I-V)
≤1µg/L
TRANSIENT
>1µg/L
DISTRIBUTION PROBLEMS
GC COMPUTER PLOT PROGRAM
MASS LOADING & STATISTICAL ANALYSIS
ENGINEERING CONSIDERATIONS (CONTACTOR MODE, HYDRAULICS, BED LIFE)
ECONOMIC ANALYSIS (CAPITAL AND OPERATING COSTS)

Figure 1. Design elements for the adsorption process.

In consideration of design, Group IA, II and III compounds should be evaluated to see if indeed they would be removed by carbon. Trace organic screening protocols are available for this task. Group IV compounds fall into a different category of concern as disinfectant type, dose and concentration are primarily used for their control. The trihalomethane formation potential (THMFP) and possibly the total organic halogen (TOX) tests can monitor this category.

Group V compounds are of concern because of their effect on Group I, II and III compounds which can be monitored by broad spectrum trace organic screening protocols. Group V compounds can be monitored by general organic parameters such as TOC since they represent 90% of the TOC (3).

This report summarizes the results of chemical (inorganic and organic) and microbiological analyses and evaluates the performance of pilot plant schemes for GAC treatment at Philadelphia. It provides a detailed analysis of the unit operations of ozonation and GAC treatment when used in combinations of O_3/GAC, O_3/SAND, Cl_2/GAC, Cl_2-O_3/GAC and no disinfection/GAC following the conventional treatment processes of raw water settling, coagulation, flocculation, sedimentation, and rapid sand filtration.

SECTION 2

CONCLUSIONS

LABORATORY OZONATION STUDIES

1- Ozone was effective in removing both natural and anthropogenic organics from Delaware River water and solutions of model compounds. TOC, UV absorbance, and specific compound chromatography were useful in monitoring this removal.

2- Ozone has its greatest effect on aquatic humus if applied before chlorination, clarification, or filtration. With respect to micropollutants, the greatest effect is in finished water. Thus for humic removal, ozone should be applied as a pretreatment, and for pollutant removal, as a post treatment.

3- In addition to organic oxidation, ozone stripped volatiles, disinfected with respect to bacteria, and added dissolved oxygen to the water.

4- Reaction rates of ozone with aquatic organics depend on the organic concentration, organic chemical structure, ozone applied dose, and ozone mass transfer in addition to matrix effects. In applying ozone, superficial gas velocity was the most important control parameter.

5- Several water quality parameters especially pH and carbonate affected ozonation of organics. The parameters were in turn altered by reaction with ozone.

6- Ozone utilized was useful in measuring the efficiency of the ozone treatment process. It may be used for determining reaction rates and stoichiometry for reaction of specific compounds or nonspecific organic parameters (e.g., TOC and A254). It may also be used for comparisons among waters of different ozone demand.

7- A protocol for laboratory testing of an ozonation system before pilot plant or larger scale operation has been developed; it may be used both as a design tool and in conjunction with control over ozonation processes.

PILOT-SCALE STUDIES

Conventional Treatment Systems

1- A portion of the dissolved organic carbon normally found in the Delaware River Estuary is readily degraded by the bacteria present in a conventional treatment train that does not include predisinfection.

2- Clarification systems can vary greatly in their ability to remove dissolved organic carbon (DOC) from their process streams. The Pilot Plant clarifier (an upflow sludge contactor without chlorination), for example, removed nearly three times the DOC removed through the Torresdale clarification system (transverse flow-through paddle flocculators and sedimentation basins with chlorination).

3- Through the postponement of chlorination until after rapid sand filtration, the Pilot Plant conventional treatment processes were able to reduce trihalomethane formation potential (THMFP) by a third during the 1-year period of study.

4- The concentrations of the specific organic contaminants in the Delaware River Estuary varied with the tidal cycle. The Torresdale Plant (which takes advantage of these tidal fluctuations by raising its intake gates at high tide and closing them near low tide) may be able to reduce the level of volatile organic compounds presently in its process water by altering its intake cycle.

5- The rapid sand filter effluent at Torresdale and the Pilot Plant was variable over time for both the compounds present and their concentrations. Twenty-two volatile organic compounds were routinely monitored. Fourteen of these compounds maintained average concentrations of greater than 0.1 ug/L.

6- GC-FID profiles from the analysis of XAD resin accumulators indicate that prechlorination at Torresdale results in the production of many more nonpolar compounds (both chlorinated and nonchlorinated). These compounds could arise from oxidation and/or substitution of low-molecular-weight organics and high-molecular-weight humics by chlorine. Thus the postponement of prechlorination should be considered for reasons other than just THM reduction.

7- The operational integrity of the Pilot Plant, a conventional treatment plant without predisinfection, was maintained continuously for more than 2 years. With a covered raw water basin, clarifier and rapid sand filters, no large algae blooms or filter-clogging bacteria were noted. However, bacterial levels were high throughout the system, and higher forms of animal life (e.g., fresh water shrimp) were occasionally observed on the rapid sand filters.

Ozonation Systems

1- The ozonation process affects the level of organic compounds in the applied water through two mechanisms: oxidation and volatilization. Stripping appears to be the dominant mechanism for the removal of the specific volatile organic compounds below a C-8 hydrocarbon (as determined by the purge and trap method for both chlorinated and nonchlorinated water). Above the C-8 hydrocarbons, stripping was predominant for the chlorinated influents but oxidation was predominant for the nonchlorinated influents (as determined by the XAD resin isolation method).

2- A by-product of the chlorination process is the production of trihalomethanes. Although very stable, the trihalomethanes are fairly volatile and are stripped from the water as it passes through the ozone contactor. 1,2-dichloropropane, as well as other volatile organic compounds, is also stripped from the process waters.

3- Although volatilization plays a major role in removing lower-molecular-weight organic compounds, it is of little significance when examining overall DOC removal. The majority of DOC removal observed during oxonation was attributed to the complete mineralization of organics to carbon dioxide.

4- Prechlorination appears to produce compounds which are resistant to further oxidation by ozone (as measured by DOC, A254 and THMFP). Therefore, oxidation of organics via ozonation is more effective when the applied water has not been prechlorinated.

5- Although THMFP levels were consistently reduced when nonchlorinated water was ozonated, the ozonation of prechlorinated water showed both increases and decreases in THMFP. Averaged through the study period, ozonation increased the THMFP levels of the prechlorinated water. This was confirmed in the laboratory-scale studies.

6- The ozonation process was found capable of converting refractory organic compounds to compounds readily degradable by bacteria.

7- Biodegradable organics, when not in the presence of a residual disinfectant, were found to be effectively removed in a sand bed with an EBCT of 15 minutes. DOC reductions can be measured through an ozone contactor (to determine the extent of complete oxidation to carbon dioxide) and through a 15 minute sand bed (to determine the extent of oxidation to readily biodegradable forms). Using this technique, it was concluded that one-fourth of the organics entering the Pilot Plant ozonator were oxidized to carbon dioxide or other readily biodegradable compounds.

8- For the oxidation of organic compounds in nonchlorinated, sand filtered water, ozone contact time was found to be a more important operating parameter than ozone dose. A synergistic effect was apparent, however, when both contact time and ozone dose were increased simultaneously.

9- GC profiles of volatile and semivolatile organics provided evidence of the production of organic compounds of unknown identity and unknown health concern during ozonation.

10- Acetone was one organic compound found to be produced at detectable levels during the ozonation process. However, since acetone is both highly volatile and biodegradable, it was not found in high concentrations in the O_3/GAC system effluents.

Adsorption Systems

General Organic Removal--

1- Typical DOC and THMFP breakthrough curves were observed for all adsorption systems. Initially, all but 5 to 15% of the applied organic loading is adsorbed onto the carbon. As the adsorptive forces diminish, a greater percentage of the applied DOC is observed in the effluent. Eventually (after approximately 9 months) a steady-state removal is achieved where between 19% and 36% of the applied DOC is removed. The degree of steady-state removal appears to be a function of pretreatment.

2- Based on DOC effluent criteria ranging from 0.5 to 2.0 ppm, preozonation significantly increases GAC bedlife. Preozonation lowers the organic loading rate onto the GAC system and produces organics which are readily degraded by the bacteria located on the GAC bed.

3- The O_3/GAC and the GAC systems all proved capable of removing odoriferous compounds from the process water. This reduction was nearly complete and appeared to be unaffected by the length of time the carbon bed remained in service, by the type of water applied, or by seasonal or temporal changes. However, while the GAC systems all proved capable of reducing the Threshold Odor Number, the use of ozone, either alone or in conjunction with GAC treatment, proved to be of little additional benefit in reducing the odor threshold.

4- A synergistic removal of DOC by the combined effect of adsorption followed by biodegradation by acclimitized microbes was not observed in the preozonated GAC systems. Therefore, the mechanism proposed to occur during the O_3/GAC process of biological activated carbon apparently does not result in enhanced removal when compared to GAC alone.

Specific Organic Removal--

1- Preozonation has no significant effect on GAC bedlife when breakthrough of the volatile, halogenated organics is chosen as the limiting criteria. Thus, a reduced loading of dissolved organic carbon (due to oxidation) and of volatile organics (due to aeration) did not result in additional adsorptive sites for the specific volatile organics.

2- Following 100% breakthrough, a 'chromatographic effect' was observed in the effluents of all adsorption systems for all of the volatile organic compounds whose average concentrations exceeded 0.1 ppb. The minimum percent of time for which a chromatographic effect was observed for benzene (17%), while the greatest chromatographic effect was for dibromochloromethane (88%).

3- The GAC systems retained all chloroform adsorbed prior to bed exhaustion. The 'net' adsorption of chloroform onto the O_3/GAC systems, however, decreased to near zero following breakthrough. This may have been due to the production of low-molecular-weight organics, as yet unidentified through the ozonation process which then compete for the available adsorptive sites.

4- General conclusions on the effectiveness of the various adsorption systems were also made by examining, as a group, the 14 specific volatile organics whose average concentrations were each greater than 0.1 ppb. An examination of the median time until the initial breakthrough of this group of volatile compounds showed preozonation to have no net effect on either plant effluent. Furthermore, the median time to breakthrough in the Torresdale Plant was 9 weeks compared to 14 weeks for the Pilot Plant. Thus conventional treatment via the Pilot Plant increased the time to initial breakthrough while preozonation showed no significant effects. These observations hold even when the compounds affected by prechlorination are removed from the sample population (i.e., the four trihalomethanes and carbon tetrachloride).

5- GC-FID profiles from the analysis of XAD resin accumulators indicate that the progression of breakthrough from all GAC systems proceeded from low to high molecular weights.

6- In general, GC-FID profiles from the analysis of XAD resin accumulators showed that preozonation had no significant effect upon the pattern of adsorption of semivolatiles during the first 10 weeks of operation. Through 17 weeks, only the nonchlorinated, preozonated GAC system exhibited a chromatographic effect for the semivolatiles.

Microbiological Considerations--

1- GAC and sand column effluents were effectively disinfected with chlorine. No bacterial regrowth was found in column effluents with an original chlorine residual of 2.0 to 2.5 ppm and pH of 8.5 after 5 days.

2- Total coliform bacteria were rarely found in the effluents of any of the GAC columns, including those systems applied with water which had received no predisinfection.

3- The most common types of bacteria isolated from the GAC column effluents included members of the genera Flavobacterium, Pseudomonas, Acinetobacter and Bacillus. Other bacteria isolated included members of the Genera Alcaligenes, Cytophaga, Acromonas and Azotobacter.

4- Pretreatment processes did change bacterial densities and genera in the influent water to the GAC columns. Chlorination effectively reduced influent densities to less than 10 per ml. The majority of bacteria which survived prechlorination were Bacillus and Flavobacterium.

5- Pretreatment processes did not influence the genera of bacteria in the GAC columns or their effluents. Temperature, however, was found to affect the composition of the bacterial communities.

6- Chlorination and ozonation significantly influenced total bacterial densities on the columns and in the effluents. Highest bacterial densities were observed on the carbon in contactors preceeded by chlorination and ozonation. The lowest bacterial populations in the effluent waters were observed in treatment trains with no previous chlorination or ozonation.

7- Actinomycetes and fungi densities decreased throughout all 5 treatment trains. Levels of less than 15 Actinomycetes/ml as a yearly average were recorded in GAC effluents.

8- Endotoxin levels in the GAC column effluents averaged 33.6 ng/ml over one year and were similar to levels found in the potable water distribution system.

9- Electron photomicrographs of the carbon particles revealed that the bacterial populations were clustered in the crevices and macropores of the carbon particle and not evenly distributed over the entire surface.

Cost Considerations--

1- For the volatile, halogenated organics (as represented by the trihalomethanes and DCP), preozonation of the GAC applied water does not result in any cost savings which would justify its use.

2- In order to maintain chloroform levels at 10 ppb, using a post-contacting GAC system at the chlorinated Torresdale Plant would cost the consumer $0.37/1000 gallons billed, or $0.23/1000 gallons treated.

3- Based on various DOC effluent criteria, GAC treatment of the nonchlorinated, Pilot Plant water was found more economical when preozonation was not employed. For GAC treatment of the chlorinated Torresdale Plant water however, a cost savings was realized when the applied water was preozonated. This cost savings was small and was not apparent when the criteria for bedlife was based on the average filter effluent removing 50% of the applied DOC.

4- The least costly means of using GAC to maintain DOC levels at 1 ppm in the chlorinated Torresdale Plant, is to incorporate an ozonation system after the Torresdale flocculation/sedimentation processes and convert the rapid sand filters to the filter/adsorber mode. The total cost for this system is estimated at $0.19 per 1000 gallons of water billed to the consumer, or $0.12 per 1000 gallons treated.

5- When THMFP is the determining criteria, O_3/GAC is generally more economical than GAC.

6- Post-filter GAC contactor construction is more costly than modifying existing rapid sand filters to accept GAC in the filter/adsorber mode.

MINI COLUMN STUDY

1- Dissolved oxygen removal cannot be used as an independent measure of bacterial activity on GAC. Dissolved oxygen removal is strongly influenced by temperature and appears to enter into a chemical reaction with activated carbon as well as biological reactions.

2- Temperature can be used to effectively reduce the rate of bioactivity on sand and GAC. Therefore, GAC applications when the temperatures are low will receive less benefit from attached bacteria than warm climates.

3- The rates of biological TOC removal on sand and GAC are approximately equal. In other words, enhanced biodegradation does not occur on the GAC granules. Therefore, sand beds were used as tools in determining the degree to which biodegradation plays a role in O_3/GAC systems studied in the pilot plant work.

4- The long term TOC removal exhibited by GAC has components both of biological removal and slow adsorption kinetics. During the TOC removal rate study conducted on ozonated, rapid sand filtered water, the contribution of slow adsorption kinetics, after 400 days on line, was greater than that of biological removal.

5- Bacteria do not appear to use adsorbed materials as substrate. Bacteria may use previously adsorbed material if some other environmental factor favors desorption back into the aqueous phase. Therefore GAC can act as a temporary storage site for biodegradable compounds.

6- Specific growth rates of bacteria on GAC contactors are initially high and decrease until steady state is obtained.

7- The use of a mass balance approach for bacterial production indicates one may even have a net death across the contactors. However, measurement of bacterial production only in terms of effluent cell concentration was found to be realtively constant. These results indicate nutrient limitation.

8- Comparison of organic substrate required for bacterial production versus TOC loss determined chemically indicate that bacterial removal is by mineralization rather than by incorporation into new biomass.

SECTION 3

RECOMMENDATIONS

Further studies are required to determine the full effect of the Delaware River Estuary tidal cycle on the concentrations of the volatile organic compounds found in the influent to the Torresdale Water Treatment Plant. Preliminary investigations appear to indicate that significant improvements can be made in volatile organic concentrations at Torresdale through alterations in the raw water intake cycle.

Besides the formation of trihalomethanes, prechlorination can produce other nonpolar organics not originally in the water being treated. For these reasons, there has been a growing concern in the U.S. over the routine application of prechlorination. The findings of this study indicate that with proper design, a water treatment plant should be able to maintain a treatment system free from the taste and odor and/or operational problems usually associated with excessive algae growth. Future studies are recommended in order to confirm these findings and to study the effectiveness of postdisinfection in waters of low turbidity and organic concentrations.

Significant stripping of volatile organics (as measured by the purge and trap method) were realized through the two ozonation systems. Reductions of over 50% chloroform were observed during the summer months. Since these reductions were attained in a system not specifically designed for stripping, it is recommended that this process be investigated at the Torresdale Water Treatment Plant for the purpose of volatile organic reductions. In developing the system costs, consideration should also be given to the part-time use of the facility, i.e., for when high volatile organic concentrations are apparent in the process water. This study should also consider the effect of aeration on taste and odor control.

The GAC systems proved capable of removing odoriferous compounds from the process water. This reduction was nearly complete and appeared to be unaffected by the length of time the carbon bed remained in service, by the type of water applied, or by seasonal or temporal change. It is therefore recommended that rapid sand filter replacement with GAC without regeneration be considered for use at Torresdale. Taste and odor studies at Torresdale are needed to define the type of odors present.

GAC has a limited bedlife for the removal of the volatile organic compounds present in trace quantities at Torresdale. Because of these short bedlives, high operating costs are associated with the use of GAC for trace organic removal. However, long-term use of GAC for taste and odor control may also provide a margin of safety in the event of an accidental spill of organics which will result in extremely high concentrations in the raw water. Studies on the effect of spills upon long term operation of GAC systems are needed at Torresdale.

The ability of a sand bed (EBCT of 15 minutes) to remove total organic carbon (when there is no residual disinfectant in the applied water) was demonstrated in these studies. A further study, comparing an ozone/GAC and an ozone/sand/GAC bed, is recommended in order to determine whether there is any synergistic effects of adsorption and biodegradation occurring during the process. Although the results of these studies indicate that there are no synergistic effects, the exact determination of this is still uncertain since there were varying levels of volatile organics applied to the GAC vs O_3/GAC systems (due to organic stripping in the ozone contactors).

SECTION 4

LITERATURE REVIEW

The use of activated carbon dates back to the Egyptian era, although the adsorption mechanism was not recognized until the 18th century (12). Its high surface area to volume ratio and surface characteristics make it an excellent candidate for adsorptive removal of a broad spectrum of non-polar organic molecules. Activated carbon has been effective as a decolorizing agent and is used extensively in the water treatment industry (as powdered activated carbon) for control of sporadic taste and odor problems. More recently, studies (13, 14) have shown that chlorination of natural background organics produces trihalomethanes (THMs) in conventional surface water treatment as practiced in the U.S. Granular activated carbon (GAC) is one treatment alternative being considered (15) for controlling both THM precursors and the THMs themselves as well as other chemicals of health concern (16). The use of GAC in potable water treatment has been the subject of a recent National Academy of Science report (9) and two symposia (17,18).

GAC STUDIES

Studies on organic removal by GAC adsorption have been conducted on three levels: laboratory scale research, using synthetic mixtures under highly controlled circumstances; pilot scale research using actual raw water sources on scaled down plants, and; full scale facilities. Research on full scale facilities has been conducted largely in Europe, where GAC filtration of potable water is more common than in the U.S.

Laboratory studies can be further subdivided into equilibrium isotherm development for single model compounds (19,20), for mixtures of compounds (21,22,23,24), kinetic studies (20,23,24,25,26) and bench top column studies (21,25,27,28,29). These have recently been reviewed (9).

The object of laboratory scale studies can be generalized into two catagories:

1) understanding the nature of solute removal by GAC
2) predicting carbon contactor performance from laboratory data.

Heterogeneity of active surface sites (19) and the distribution of pore sizes in GAC (30) along with interaction between solutes (24,29) generates extreme complexity in understanding the nature of GAC adsorption. The presence of micro-organisms on the GAC surface (31) adds to the complexity. Several models are available to predict carbon contactor performance (e.g. 27,32,33). These models differ in their approach to the mechanism of long term organic removal. Proposed mechanisms of long term organic removal will be discussed later.

The complexity of removal processes on GAC and uncertainty of some aspects of the underlying mechanisms, in combination with the variability of organics found in surface waters, has led to pilot studies in lieu of accurate models. Research at Philadelphia (summarized elsewhere, (25)) began with laboratory studies (25,29) and pilot studies (34,35). One result of the first pilot study (34,35) was an indication that the post adsorber mode of GAC was most desirable. Subsequently, a second pilot study was conducted to evaluate various empty bed contact times (EBCT) and superficial flowrates (36). Using chloroform removal as a criteria, no difference in removal efficiency was observed, as adsorptive capacity of a carbon contactor for chloroform was directly proportional to EBCT (36). Total organic carbon (TOC) removal was a function of EBCT, with higher TOC removals per gram of GAC on columns with longer EBCTs.

Another pilot run at Philadelphia (37) focused on the effects of aqueous chlorine on the removal of organics. Oxidation of the carbon's surface has been shown to reduce adsorption capacity (25,29). This run also analyzed specific organic removals as well as TOC and chloroform (38). Long term TOC removal was observed in both the second and third pilot runs, with bacterial activity being suggested as the mechanism. This long term TOC removal phenomena is common to other pilot plant facilities in the U.S. (39) and Europe (40).

Several pilot plant evaluations have been conducted with wastewater (41 to 44). While not directly applicable to potable water treatment, these studies gave initial insight into the potential magnitude of bacterial activity on GAC. In these studies, carbon removed more TOC than predicted from isotherm studies, and in some cases the mass removed exceeded the mass of GAC.

Full scale applications of GAC have occurred predominantly in Europe (33,45,46). These plants have been designed for taste and odor control, and monitoring of the treatment process usually involves an indirect measurement of TOC through UV absorbance. Although the treatment goals are not as closely related to specific organics as the proposed U.S. regulations (16), these plants give a baseline of operating data for full scale plants. High bacterial densities on GAC and quasi-steady state TOC removal after initial breakthrough are common to all potable water treatment plants using GAC in Europe (9).

OZONATION IN WATER TREATMENT

The use of ozone in potable water treatment has been the subject of several recent reviews (47,48), a book (49), and two symposia (50,51). Only those applications of ozonation directly relevant to this project will be discussed here. Some of the functions of ozone in drinking water treatment which depend on its oxidative as opposed to disinfective properties are shown in Table 2.

TABLE 2. OXIDATIVE FUNCTIONS OF OZONE IN WATER TREATMENT

Oxidation of Inorganics

- soluble metals
- cyanides
- ammonia

Oxidation of Organics

- color removal
- organoleptic reduction
- oxidation of micropollutants
- enhancement of biodegradability
- destruction of trihalomethane precursors

The source of color in water is often humic materials (52) or complexed metals. These materials contain conjugated double bonds that are readily attacked by ozone (53). The use of ozone in decolorization of drinking water has been discussed by Schwartz & Moncrieff (54) and will constitute a portion of the current investigation.

Numerous micropollutants are capable of being destroyed by ozone (50,55). In general, those compounds which are highly oxidized will be refractory to ozonation. This includes carboxylic acids, chlorinated materials, alkanes and some aromatics. Materials containing double bonds or other sources of high electron density such as olefins or activated aromatics are highly ammenable to ozonation.

Ozone has been used in several cases to enhance biodegradability especially in the so-called biological activated carbon (BAC) process (56, 5). In this process, ozone is utilized to convert biorefractory materials into microbally utilizable substrate. Colonies of micro-organisms which reside on granular activated carbon contactors in a water treatment plant are then able to utilize the substrate and remove the organics from the water. Ozone has also been used as a pretreatment to enhance biodegradability in biological treatment processes (57).

The effect of ozone on trihalomethane precursors has been reviewed by Rice (48). In a total of 23 investigations, the trihalomethane formation potential was decreased in 16 cases, raised in 6, and remained unchanged in one after the application of ozone. These effects were found to be related to ozone dose, contact time, pH, nature of the precursor substrate, and composition of the matrix. Hoigne (58) has advanced the hypothesis that the change in formation potential is related to the chemical mechanism of the ozonation reaction. If the humic precursor is represented as a hydroxylated aromatic, a free radical reaction by ozone will lead to an increase in formation potential where a direct reaction will lead to a decrease. In order to explore these topics and related materials in greater detail, the reaction chemistry of ozone, ozonation of aquatic high molecular weight materials, ozonation of micropollutants, kinetics of ozonation, ozone mass transfer, and concepts of ozone demand will be considered in subsequent sections.

Ozone Reaction Chemistry

Ozone is unstable in water and it is this property which often determines its mechanism of reaction. The net products of ozone decomposition are oxygen and small amounts of hydrogen peroxide (59), however, many reactive intermediates are also formed in the process:

$$O_3 + OH^- \dashrightarrow O_3^- + OH^\cdot$$

$$O_3 + H_2O \dashrightarrow O_2 + 2OH^\cdot$$

$$O_3 + OH^\cdot \dashrightarrow O_2 + H\dot{O}_2$$

$$2H\dot{O}_3 \dashrightarrow H_2O_2 + O_2$$

Decomposition is catalyzed by hydroxide ions (high pH) and a mechanism has been proposed to account for this (60). Peleg (59) has reviewed the reactivity of the various intermediates and found hydroxyl radical to be the most reactive. Hoigne and Bader (61,62,63) have performed extensive research on this system and demonstrated that, in an alkaline medium, the reactions of ozone with organic substances are occuring through both hydroxyl radical and direct ozone mechanisms. In their reaction scheme, ozone entering water may be physically stripped, may react directly with substrate to form an oxidized product, or may enter into a series of radical reactions. In the radical pathway, ozone is converted to hydroxyl radical by reaction with hydroxide ion or another free radical after which it reacts either with the intended substance (substrate) to form an organic radical or with an extraneous material (radical scavenger) such as carbonate ion. The organic radicals formed will react with the solvent (water) to form an oxidized product. Hoigne & Bader (63) have determined that the rates of the free radical reactions are several orders of magnitide faster than the direct reactions, thus, if both processes are occurring simultaneously, only the radical reaction will be observed. The pH dependence of the ozone decomposition process suggests that, in acid medium, the reaction mechanism will be primarily direct or ionic, whereas in base it will be via the radical pathway.

The reactions of hydroxyl radicals with various substrates are well documented (64). These species have also been detected in natural waters (65) which may be related to the free radical nature of aquatic humics and the reactions between humics and ozone.

The ozonation process itself is stepwise and therefore product formation is as much a function of time as it is of the actual chemical mechanism. If the ozonation reaction is stopped at a given point, numerous products may be isolated depending on what has reacted and what has already formed. This fact has led several investigators to follow the production of products of ozonation along with disappearance of substrate as a function of time. Gilbert (66) has accomplished this with a large number of compounds. In these studies, he postulates probable products based on known mechanisms and then follows their ozonation along with disappearance of the substrate. Information such as is revealed by these "time concentration" plots appears to be considerably more valuable than results of investigations that merely list products formed on ozonation.

There is currently a good deal of emphasis on research into products of ozonation due to the fact that researchers want to be able to avoid the ozone counterpart of trihalomethanes when ozone is used in potable water treatment. These studies have been reviewed by several authors (9,66). This topic has also been the subject of a symposium (67). As may be expected, the final products of ozonation are, for the most part, low molecular weight, highly oxidized species. Dibasic carboxylic acids, monobasic acids, oxyacids, and carbonyl compounds appear in every investigation reviewed.

Ozonation of Aquatic High Molecular Weight Materials (Humics)

With the exception of the fact that the process is heterogeneous, the reactions of ozone with aquatic humus should be similar to the reactions of humus with other strong oxidants. Since ozone and its decomposition products are stronger oxidants than most other agents used in water treatment or in the laboratory for degradation studies, ozone should be able to oxidize more species than others and kinetically controlled reactions should be faster. This is supported by studies of oxidation of phenol where the rate of reaction is proportional to the electromotive potential difference between the oxidant and the organic substrate (68).

The oxidative degradation of humic materials has been reviewed by several authors (69,70,71,72). The molecular basis of oxidation is loss of electrons and consequent cleavage of chemical bonds in the substrate. With respect to humus, the net results usually are loss of bulk properties such as color, UV absorbance, fluorescence, often a decrease in molecular weight, and the formation of highly oxidized molecular species. In addition to chemical oxidation, the effects of ultraviolet radiation on fulvic acid have also been studied (73). Since ultraviolet radiation reacts with water (203) forming hydroxyl radicals in a manner similar to that of ozone decomposition, the effects should be qualitatively similar to ozone reactions expecially at high pH values. These authors found that the fulvic acid was readily mineralized and the chromophores destroyed.

The effects of oxidants used in water treatment have also been studied with regard to their reactions with humus. Mallevialle (74) compared the reactions of chlorine and chlorine dioxide on humics and found that they both reduced color, fluorescence, and TOC although chlorine dioxide did not form trihalomethanes whereas chlorine did. Gjessing (71) found that hydrogen peroxide and ultraviolet radiation was especially effective in removing humus from waters as followed by non-specific analytical parameters. Permanganate oxidation has also been studied in the water treatment situation (75) and found to reduce color and trihalomethane formation potential by oxidation of humus.

In 1963, Black and Christman (52) ozonated aquatic humic material which had been isolated from water and concentrated. They found that ozone reduced both the color and the chemical oxygen demand of the sample and demonstrated that color removal did not correspond to total mineralization of the organics.

Gjessing (71) ozonated several samples of aquatic fulvic acid and confirmed the removal of color and COD. He also used gel permeation chromatography and concluded that ozone was capable of breaking up large organic moities into smaller ones. This work has lately been confirmed by Glaze and colleagues (76).

Mallevialle investigated the reaction of ozone and aquatic humics in some detail (77). He studied the effects of ozone on humics by measuring color, TOC, TOD and polyhydroxy aromatics as a function of time. Based on these measurements, he proposed a rate law in which disappearance of substrate as measured by TOC was pseudo first order. He additionally found that the humic concentration declines must rapidly when monitored by polyhydroxy aromatics (Folin's test) followed by fluorescence, UV at 254nm and TOC. Ultrafiltration experiments revealed that ozonated humics were of lower molecular weight than the untreated material.

Kimes and Taylor (78) ozonated natural aquatic humics and found color removal to be first order with respect to substrate concentration. Van Breeman and coworkers (79) investigated reactions of ozone and fulvic acid in the context of water treatment. They used a type of ozone demand measurement and found that color, DOC, and TOC were independent of ozone contact time and dose. Peel and Benedek (80) found that the ozonation of humics was first order with respect to TOC removal and that ozonation increased the biodegradability of the humics. Gilbert (81) fractionated humus by ultrafiltration and ozonated the separate fractions. He found that ozone decreased molecular size and increased biodegradability. Additionally he found that the various fractions exhibited different stochiometries and kinetic curves (time-concentration plots). Several studies have also taken place on the products of ozonation and humic materials and are reviewed elsewhere (9,47).

Considerable work has also been accomplished in the area of reactions of ozone with lignin. Lignins are similar to humic material in structure and properties and may themselves constitute a fraction of the high molecular weight organic component of natural waters (82). Melnyk and Netzer (83) studied the reactions of ozone and lignin in pulp mill effluents and derived a first order kinetic model. This group (84) also used kinetics in design of an ozonation process and demonstrated the importance of mass transfer in the reactions of ozone and lignin. Bauman and Lutz (85)showed that the amount of color removal by ozone was a function of only the mass of ozone reacted and not the ozone applied dose. Jurgensen & Patton (57) used ozone to successfully enhance biodegradability of lignosulfonic acid when the reaction was conducted under basic conditions.

Ozonation of Aquatic Micropollutants

As noted above, ozone has diverse applications in terms of oxidizing organic substances. In general, activated aromatic, alkyne, and compounds containing activated olefinic bonds are extremely labile to ozone oxidation. Alkanes, alcohols, carboxylic acids, and highly chlorinated organics tend to be refractory to ozonation or when the application of ozone is coupled with UV radiation.

The reactions of ozone and micropollutants have been recently reviewed (9). The compounds investigated included benzene and related polynuclear aromatics, pesticides, humic acid, chlorinated and unchlorinated phenols. With the exception of malathion and parathion, which may be removed if additional ozone is applied, most substrates were oxidized to compounds less hazardous to human health than the starting materials.

Ishizaki and co-workers (86) undertook an investigation of a series of priority pollutants and known toxic substances for their susceptability to ozonation. Emphasis was placed on compounds which could bioaccumulate. Ozone was found to be excellent for the removal of the pollutants as represented by COD and BOD. Compounds which were well degraded were nitrobenzene, dimethylphthalate, triethanolamine, 1-napthol, benzidine, n-nitrosodiphenylamine, phenol, and benzothiazole.

A comparison of oxidation by chlorine, permanganate and ozone was performed for specific organic removal from drinking water in Philadelphia (87). These researchers concluded that pollutant removal by ozone was significant and warranted further investigation. Chlorine and permanganate oxidation were not efficient for the removal of aqueous organic pollutants.

The ozonation of aniline, phenol, and phenoxy acetic acid herbicides (88) indicated that ozonation of an aromatic ring is a two step process. The first step is a fast reaction leading to opening of the ring. The second and slower step leads to the formation of oxidized aliphatics and other degradation products. This study also involved biodegradability and production of halogenated volatile organics upon chlorination. It was found that ozone enhanced the biodegradation of the aromatic compounds studied. The oxidized aliphatics produced demonstrated less reactivity to chlorine than the starting materials.

Treatability studies for five carcinogens were performed employing ozonation, biodegradation, and carbon adsorption (89). The compounds considered were napthalene, 1,1-diphenyl hydrazine, B-napthylamine, 4,4-methylene-bis(2chloroaniline), and dimethylnitrosamine. Ozonation was effective in removing the carcinogens with the exception of dimethylnitrosamine.

Erb and colleagues (90) ozonated phthalate esters, pesticides, herbicides and polychlorinated biphenyls in distilled water and natural water matrices. The natural waters included a surface water, a ground water, and water processed for drinking. In all instances, the rate of removal of the compound was slower in the natural water matrix than in a pure aqueous solution.

The review of the literature indicates no water treatment plants currently utilizing ozone expressly for micropollutant control. It should be realized, however, that ozone is a multifacted tool in water treatment and apart from its primary purpose may often produce secondary beneficial results. Thus ozone applied for purposes of disinfection or metal oxidation will also act to oxidize micropollutants, render high molecular weight materials more biodegradable, and raise the dissolved oxygen content of the water.

Ozone Mass Transfer and Reaction Kinetics

In chemical engineering practice the time to accomplish a process is the key factor in design of equipment to carry out the process. Since the reaction of ozone and aqueous materials is heterogeneous (i.e. ozone in the gas phase must be transferred into solution prior to reaction), not only the kinetics of the actual chemical reactions, but also the process of mass transfer itself must be considered. If the rate of mass transfer of ozone into solution is a slower process than the rate of the chemical reaction, mass transfer will limit the rate of the overall process, and optimization of mass transfer must be taken into account in design of process equipment.

Several theories have been proposed to describe the transfer of ozone into the aqueous phase notably the two-film model, penetration theory, and surface renewal theory (91). Transport across boundaries is generally governed by the molecular property of diffusion and the magnitude of the concentration gradient across the interface as stated by Fick's first law. In the two film theory, the interface between the water and the gas stream is thought to consist of a water film and a gas film. Diffusion in the gas film is very rapid and thus, slower diffusion in the liquid film dominates in controlling overall mass transfer. The two-film theory in the absence of chemical reaction leads to the equation:

$$N_a = k_La(Cs-C)$$

where N_a is the flux of ozone across the interface
k_La is the mass transfer coefficient which in essence is a rate constant for mass transfer.
$Cs - C$ is the concentration gradient driving force.

The factors which most influence mass transfer from the gas to the liquid phases are bubble diameter and agitation. Small bubbles are far superior to large bubbles (92,93). The bubble size in turn is dependent on several primary factors including the direction of flow (co-current, countercurrent, or semibatch) in the contactor and the velocities of flow. In a continuous system, bubble diameter is largely determined by liquid flow, while in a semi-batch system, it is the flow rate of the gas (94,95). Increased agitation has been shown to linearly increase ozone mass transfer. Other factors include solution viscosity, temperature, and the presence of surfactants. These factors act by influencing the mass transfer coefficient. Overall mass transfer of ozone can also be influenced by affecting the (Cs - C) term. This can be achieved by increasing the ozone applied dose or by intermittant addition of ozone into the solution (96).

Several authors have derived and discussed models for ozone mass transfer. Danckwerts (91) discussed mass transfer and diffusion with and without chemical reaction. Heist (93) reviewed mass transfer and chemical kinetics in ozone reaction with wastewater. Roustan and Mallevialle (97) have taken the basic theory and applied it to use of ozone in water treatment with and without chemical reaction. Several other models including those of Majumdar et.al. (98), Lee (99) and Hill & Spencer (92) have also been used.

Several rate laws for reaction of ozone with pollutants, especially phenol, have been noted in the literature which are highly dependent on ozone mass transfer. In some cases the effect of mass transfer was implicit (100) or explicit (101). The importance of mass transfer in any ozone reaction should not be underestimated. Quantification of the parameters involved in mass transfer will allow for a greater degree of control over the ozonation process and more effective design of equipment in water treatment.

Quantification of Ozone Demand

In the design of a conventional potable water treatment plant, the determination of the chlorine demand of the water is an important consideration (102). This parameter measures the difference between the applied chlorine dose and the amount of measurable chlorine either free, combined, or total at the end of a specific reaction period. It serves as the basis for the specification of chlorination equipment during the design phase and for successful control over the chlorination unit process during plant operation. Procedures for quantification of chlorine demand have been evolved (103) and are used on a routine basis by water treatment plant operators.

In contrast to chlorine, analogous procedures and definitions for ozone have not been developed. This is probably due to the various problems associated with mass transfer, the complexity of ozone reaction chemistry, and the high degree of operator sophistication necessary for performing ozone analyses both in the gas phase and in solution.

A review of the literature indicates that four primary ozone demand techniques are available. These include two methods of Legeron (104), the "ozone utilized" concept of Breitbach and co-workers (105) and the "oxidation competition value" of Hoigne and Bader (106). The first two techniques involve contacting ozone in the gas phase with the target water in specially designed glassware. After a given reaction time, ozone residuals are analyzed and the ozone demand calculated on the basis of the difference between ozone applied and the residual remaining. In the ozone utilized concept, a sample of the target water is ozonated in a contactor designed to simulate the ozone reactor in a water treatment situation. A mass balance is constructed with respect to ozone and the ozone utilized calculated as the difference between the ozone applied dose and the sum of ozone exiting with the off gases and ozone left in solution. The oxidation competition value is based on the differences of reaction rates of ozone with a reference solute under different conditions. As the ozone demand of the water increases, the difference in reaction rates will also increase as the ozone is consumed by materials other than the reference solute.

The ozone utilized technique is the only one that accounts for mass transfer. The oxidation competition value is, however, fundamentally related to ozone reaction chemistry and could have broad application.

OZONATION AND GAC

The combined unit processes of ozonation followed by GAC adsorption have been extensively reviewed by Miller and Rice, et al (5,56). These papers concentrated mainly on operating full scale utilities. Several authors have observed increased biodegradability of humic acids (77), potable water (4), and wastewater(107) upon ozonation. A detailed study on the effects of ozonation on biodegradability and adsorbability was conducted on three waters (28,108). This study concluded that ozonation improved biodegradability for two of the three waters studied (natural plus synthetic organic polluted river water and river water containing high levels of natural organics). Furthermore, ozonation did not consistantly alter adsorptivity. Previous work (4) had concluded that adsorptivity was reduced following ozonation. A further aspect of the ozone-GAC process is the proposed synergistic action for organics removal. This will be discussed in the next section on mechanisms for TOC removal on GAC.

TOC REMOVAL

TOC reduction across an activated carbon contactor has been widely employed to assess carbon contactor performance (36,38,39,40,41,44,45). All GAC studies using natural water sources have a common pattern for TOC removal. There is initial leakage of organics through the GAC bed followed by slowly increasing effluent concentrations until an apparent steady state removal is reached. Reducing the concentration of TOC in water is not a primary concern in U.S. water treatment goals. However, TOC has been correlated with trihalomethane formation (109), although this type of correlation has not been shown to be significant elsewhere (110). Furthermore, competition for adsorption sites between natural background organics and specific solutes has been demonstrated (24,111). Therefore, reducing the load of TOC onto the GAC may extend the useful life of the GAC for removal of health related organics.

Two current theories used to explain the long term TOC removal are biological removal (27,112,113) and slow adsorptive kinetics (32,33). The use of micro-organisms on the GAC to help remove TOC is of particular interest because it may be enhanced through the use of preozonation.

Biological Regeneration

The occurrence of large numbers of bacteria on GAC filters has been well documented (31,114). In chlorinated treatment plants, bacterial densities are much higher in the effluent than in the influent of a carbon contactor. This increase has been attributed to removal of chlorine and other toxic materials by the top of the GAC column, concentration of organics on the carbon surface, adsorption of bacteria by GAC and a "sheltered" environment in the macropores of the GAC which shields bacteria from shear forces. These same factors apply in a non-chlorinated system.

Enhanced biodegradation of organics on GAC is proposed to occur due to acclimization of the microbes to adsorbed substrate (27) resulting in greater biodegradation than on inert media. In this proposed complex process, GAC adsorbs recalcitrant organics as well as bacteria. Thus, the carbon keeps the bacteria in contact with higher concentrations of refractory organics than in the bulk liquid. Maintaining contact between bacteria and adsorbed recalcitrant organics allows the bacteria to acclimate to the recalcitrant organics. Biological regeneration emphasizes that the solute must be adsorbed first (112,113). The bacteria then use a portion of the retained organics, opening sites on the GAC for further adsorption of other organics.

The action of GAC in adsorbing organics would decrease the aqueous phase concentration of organics and logically, this would inhibit the acclimization of bacteria to adsorbed substrate. Thus, acclimization has been referred to as a common fallacy in activated carbon adsorption theory (115). Typically, in a real situation, the influent concentration of organic compounds is variable. Some of the time, carbon is adsorbing the organic in question, but when the influent concentration drops to a low or zero value, the GAC may release the organic. In this case, carbon acts as a buffer for bulk phase concentration of an organic which has a rapidly varying influent concentration and acclimization of bacteria is possible on GAC whereas on an inert substance such as sand, acclimization is less likely due to the sporadic appearance and disappearance of the organic in the aqueous phase.

Improved biodegradability of naturally occurring TOC has been observed following ozonation (4,28,108). Therefore, the interaction of ozonation and GAC unit processes may be engineered to maximize the long-term TOC removal capability. It is proposed that carbon bed life can be prolonged by converting a portion of the recalcitrant organics to biodegradable organics in the ozonation process (112). The attached microbes then convert the biodegradable portion to biomass, carbon dioxide and waste products. The TOC which is converted to biomass or carbon dioxide does not take space on the GAC. Other biological end products may or may not adsorb, but the net result is less TOC which is adsorbable.

Slow Adsorption Kinetics

The long term removal of TOC by GAC can be alternately explained by a dual rate kinetic model (32,33). Two disticnt stages of adsorption have been observed during batch equilibrium studies (20,23). In the first stage, rapid adsorption in 50%-80% of the total carbon capacity is observed within a few hours. The remaining capacity is exerted very slowly. The dual rate kinetic model takes both stages into account and predicts the quasi steady state removal so commonly seen on GAC for lumped parameters such as TOC.

The model of activated carbon considers, as a first approximation, two types of pores. Macropores are defined as those pores in which diffusion rates are unhindered by the pore walls and micropores are those pores with radii of comparable size to the diffusing species (32). Because of strong multidirectional adsorptive forces in micropores and the restricted diffusion rates caused by the proximity of the pore walls, transport rates are considerably lower than in the larger pores. The rapid initial uptake rate in batch isotherms, and large initial removals encountered in column studies are assumed to occur in the macropores. The slow approach to equilibrium after initial uptake observed in batch studies, and the quasi steady-state removal seen in column studies are attributed to the micropores.

MICROBIOLOGICAL STUDIES ON GAC

The occurrence of high population densities of bacteria on GAC has been well documented (31,56,57,114,116,117). Several researchers (118,119,120) have found that the standard plate count (103) is inadequate for studies involving GAC. In general, the use of a seven-day incubation, 28°C incubation temperature and soil extract agar media (120) yield bacterial counts approximately two orders of magnitude greater than the standard plate count technique. The details of the soil extract method were developed in the present study and will be detailed in the Experimental section.

The general characteristics of bacterial populations growth (116,118) on the carbon and in the water following contactors is as follows: Bacterial densities in the initial effluent are quite low, due presumably to disinfected influent. Densities in the effluent increase dramatically until they reach maximum counts, then decline to a relatively stable density (118) of slightly less then 10^5 bacteria/ml. Densities on the GAC are approximately 100 times greater than in the water on a volume basis (118).

The relationship between bacterial density and TOC removal has not been well defined. Parsons, et al, (121) found no correlation between bacterial densities and TOC removal. However, that study only lasted two months. Werner, et al, (122) reports that while the GAC is operating predominantly in the adsorptive mode (as would occur when carbon is initially operating), bacterial removal of TOC may be suppressed. Eberhardt (113) suggests an equation for design of a biological activated carbon filter which does not contain terms for bacterial density, but rather a lumped parameter called specific filter efficiency. When comparing efficiencies for activated carbon (1g DOC/m^3/hr) to that of a slow sand filter (0.02 g DOC/m^3/hr), Eberhardt concludes that biological activity is greatly accelerated on GAC.

Several past studies have used dissolved oxygen removal as an indirect measure of biological activity (28,31,122). Increased oxygen consumption was viewed as purely biological. However, Prober, et al, (123) has shown that dissolved oxygen reacts directly with the carbon surface. Only a small percentage can be recovered from the surface and surface oxides increase following reaction with dissolved oxygen. Furthermore, all studies by Prober showed oxygen consumption up to the end of the study, with the longest study reaching 1700 hours. Thus, chemical interaction between GAC and oxygen, and oxygen consumption by bacteria are difficult to separate, making studies involving dissolved oxygen consumption difficult to interpret.

MICROBIOLOGICAL STUDIES ON INERT MEDIA

A review of microbiological activity on inert media will help determine whether the activation process on GAC offers any bacterial advantage to less expensive and hardier granular materials such as sand. Zobell and Grant (124) and Heukelekian and Heller (125) have investigated bacterial utilization of low concentrations of TOC in the presence and absence of granular media. Zobell's results indicate that at organic concentrations of less than 10 mg/l, bacterial removal of TOC is proportional to the initial concentration of TOC and independent of bacterial density. Furthermore, he noted that at low concentrations, a greater proportion (i.e., more than 60%) of the organic carbon is mineralized (converted to CO_2) than in environments in which high food concentrations are available.

Heukelekian and Heller (125) were investigating the common "bottle effect" observed in microbial studies in which bacterial densities increased in small containers more so than in large containers. They found that by increasing the surface area available to bacteria (by adding glass beads), the bacterial density becomes independent of substrate concentration below a concentration of 25 mg/l. Below 5 mg/l, the bacterial density in the container with glass beads become relatively constant at 10^4 cfu/ml.

McIntyre, et al, (126) investigated the activity of bacteria in a sand ecosystem. Bacterial counts were determined to be 10^8 - 10^9 "bacterial like objects" per gram of sand. The soluble organic carbon in this ecosystem ranged from 2 to 5 mg/l but consistantly hovered around 3 mg/l. Thus, large populations of bacteria can develop in natural environments of low organic concentration.

Van der Kooij (119) found bacterial densities on the order of 10^6 to 10^7 cfu per ml of sand on filter fed tap water (TOC = 3 mg/l). The densities were an order of magnitude less than on activated carbon. In a second publication, Van der Kooij (127) shows much less difference in densities on sand and GAC (although GAC had consistantly greater densities). Van der Kooij attributes the greater density on GAC to greater surface area on GAC compared to sand.

TEMPERATURE EFFECTS

The response of most reactions to temperature fluctuations has been found to be well represented by Arrhenius' law (128). The application of this law to these studies can be found in the section on Description of Studies. Temperature affects the rate of reaction and the extent of adsorption (129). The extent of adsorption increases with decreasing temperature but the rate of diffusion decreases with decreasing temperature. The net result is that normal temperature variations have only a minor effect on adsorption (129).

Biological reactions generally double in rate over a temperature differential of 10°C. Stephenson (130) measured the effect of temperature on

Escherichia Coli using various single substrates and a temperature range of 23°C to 33°C. he found an average ratio of 2 for single substrate, single organism reactions. In a mixed (activated sludge) system, the ratio of reaction rates has been measured as low as 1.35 (131).

The effects of temperature on diffusion and biodegradation are discussed in more detail in the Description of Studies. Generally, physical mechanisms such as diffusion show little temperature dependency; biological reactions show greater dependency; and chemical reactions can show the greatest effects, depending on the activation energy.

Hoppe (132) reports on the activity of bacteria in the Baltic sea and shows a very large ratio (36:1) for uptake of radio-labelled amino acids (summer rate: water rate) and less of a ratio for numbers of active bacteria (8:1). The temperature range for this data was 2°C to 20°C. In terms of the reaction rate per bacteria, this is greater than doubling the rate per each 10°C change in temperature. Hoppe suggests that in cold seasons more bacteria are required to mineralize a certain amount of substrate than in warm environments. Conversely, the same amount of substrate can support more bacteria in cold environments.

SECTION 5

DESCRIPTION OF STUDIES

Three major areas of study were investigated to understand the use of both ozone and GAC for water treatment. These were:

1) laboratory scale studies of the ozonation process;
2) pilot scale studies of the ozone/GAC process; and
3) mini-column studies which examined mechanisms for long term TOC removal.

OZONATION STUDIES - LABORATORY

The overall objective of the laboratory ozone study was to develop an understanding of the ozone process for treatment of drinking water. This includes development of a laboratory protocol which could be used to observe the effect of ozone treatment prior to large scale operation.

The specific ozone studies are broken down into the following areas:

1) ozonation of Delaware River water at various stages of treatment; also ozonation of high molecular weight materials (humics) which represent about 90% of the total organic carbon present in the river water (3);

2) investigation of ozone utilized for assessing ozone demand; and

3) ozonation kinetics of different substrates present in the water.

In general, the studies focused on ozonating a series of materials in a semi-batch contactor under a rigorously controlled set of conditions and investigating the effect of ozone on different parameters. Numerous peripheral studies were also performed to further clarify issues raised in the initial studies.

Ozonation of Delaware River Water

Ozonation of Delaware river water was intended to ascertain certain specific pieces of information: the use of the several non-specific parameters as monitoring techniques in ozonation, the optimal point of ozone application, design information relating to ozonation equipment, and the effect of ozone on water quality parameters. Delaware River water with three levels of pretreatment were investigated: raw water, water that had been chlorinated and clarified at the Torresdale Plant, and finished process water. Monitoring techniques was disinfection (as determined by Standard Plate Count), trihalomethane formation potential (THMFP), dissolved organic carbon (DOC), and UV absorbance at 254 nm (A254). Ozone was applied in two different doses, at two different contact times, and with oxygen as a control.

In the study of the ozonation of Delaware River water, various samples of water were ozonated and the concentration of the parameter under investigation was measured before and after treatment. These included investigatons at higher, non-ambient concentrations, investigations on simulated water solutions, and investigations where the concentrations were controlled.

The investigation of the ozonation of high molecular weight organics (humics) was undertaken to ascertain the optimal conditions for rendering refractory materials biodegradable by ozonation. Although biodegradability itself was not studied in this part of the project, the focus was on the physical and chemical routes by which ozone was utilized by the humic materials. The reaction was approached as if it were an ordinary chemical reaction taking place in a manufacturing situation with the goal being the manufacture of low molecular weight organic substrates.

It was realized early on in the investigation that there were several problems inherent in using humic materials from the Delaware River as part of the study,including preservation,concentration and lack of reproducibility. In order to circumvent these problems, it was decided to use concentrated aquatic humics from Delaware River in addition to model compounds and humic analogs. It was determined more relevant for Pilot Plant operation to establish control and understanding with respect to the reaction process than merely to generate lists of ozonation products which would probably not be reproducible if conditions of ozonation were changed.

Ozone Utilized

A study of ozone demand was undertaken in order to provide the ozone analogy of chlorine demand for use of ozone in potable water treatment. The concept of ozone utilized was used to obtain a mass balance with respect to ozone. Experiments investigated interferences by chlorine and the effects of ozone applied dose, pH, buffer composition and substrate concentration.

Ozonation Kinetics of Different Substrates

The investigation of the reaction of ozone with high molecular weight organics, analogs and micropollutants had two main foci: first, the reaction itself, and, second, the effect of the ambient water matrix on this investigation. Although the primary use of ozonation in this project is the synthesis of utilizable substrate, it must be realized that all the side effects of ozonation will also be expressed throughout the course of treatment. Since one of these is removal of micropollutants, it was felt important to investigate this with a view toward optimization of this process.

Spectroscopy as an Ozonation Monitoring Technique

A study of the ultraviolet/visible spectra of high molecular weight aquatic organic substances was undertaken in order to gain a better understanding of spectroscopy as a tool for following the course of ozonation. These studies included Lambert-Beer law observations, effect of scattering versus absorbance of light, and correlations between spectroscopy and other non-specific parameters.

PILOT PLANT STUDIES

Five (5) advanced water treatment (AWT) systems were evaluated in this study to determine their relative effectiveness for removing trace organic compounds from conventionally treated Delaware River water. Four of the five systems tested were granular activated carbon (GAC) systems; one preceeded by ozonation (O_3/GAC), another by chlorination (Cl_2/GAC), a third by both (Cl_2/O_3/GAC) and a fourth by neither (GAC). The fifth system was a sand bed preceeded by ozonation (O_3/SAND).

Conventional Treatment Train

Of the five AWT systems tested, two received their water from the chlorinated rapid sand filter effluent of the Torresdale Water Treatment Plant, a conventional coagulation/filtration plant which supplies the City of Philadelphia with one-half of its daily water requirements. The remaining three AWT systems received non-chlorinated rapid sand filter effluent of a 30,000 GPD pilot plant. The Pilot Plant was designed and built in 1976 to offer a high degree of flexibility for investigations of new and conventional water treatment techniques. Table 3 compares the operating characteristics of the conventional treatment trains of the Torresdale and Pilot Plant during the period under investigation. Possibly the most important of the many similarities between the two plants, are that they draw their influent water from the same point along the Delaware Estuary, and that they both coagulate, settle and filter their water. The primary difference between the operations of the plants is the fact that only the Torresdale Plant chlorinates its process water; the Pilot Plant does not practice disinfection in any manner. The purpose of using the two plants was to determine the effect of chlorination and chlorine by-products on the AWT systems investigated.

Torresdale Plant Description--

The Torresdale Water Treatment Plant (Figure 2) has its intake system on the 110.5 mile point of the Delaware River Estuary in Northeastern Philadelphia. Water flow into the plant is by gravity and is subject to the tidal cycle of the river. The water temperature variation during this study is shown in Figure 3. Upon entering the raw water sedimentation basin, the water passes through both coarse and fine screens for the removal of debris from the river and is disinfected for the purposes of bacterial and algae kill and for the control of taste and odors. Typically in the past, continuous chlorination to breakpoint was the primary means to achieve these goals. However, with the recent concern over the production of trihalomethanes in the water treatment plant and the advent of federal regulations governing maximum contaminant levels (MCLs) for trihalomethanes in drinking water, prechlorination at the Torresdale Plant intake has ceased. Instead, occassional 'shock' treatments of the incoming water with chlorine dioxide are used for the control of taste and odor and microorganisms. The detention time in the

TABLE 3. CONVENTIONAL TREATMENT PLANT COMPARISONS

	Torresdale Plant	Pilot Plant
Average Flow	230 MGD	30,000 GPD
Source	Delaware River	Same
Intake Frequency	Tidal Cycle-Every 6 Hours	Continuous
Raw Water Basin	18 Hours Detention Time	12 Hours Detention Time
Coagulant	Ferric Chloride	Same
pH Adjustment	Lime	Sodium Hydroxide
pH	8.5	8.5
Clarification	Horizontal-Flow Through Paddle Flocculators & Sedimentaiton Basins	Upflow Sludge Contactors
Filtration	94 RSFs - 1041 ft^2 each	2 RSFs - 5 ft^2 each
Chlorination	Breakpoint at rapid mix; 1.5 to 2.0 ppm free Cl_2 residual applied at RSFs	None
ClO_2 and $KMnO_4$	Occasional* (at plant intake)	None
PAC	Occasional* (at rapid mix)	None
Aeration	None	Occasional* (at rapid mix)
Ammoniation & Fluoridation	Post Treatment**	None

* See Figure 5

**Torresdale water to be applied to the AWT systems is drawn from the RSF effluents, prior to ammonia and fluoride addition.

Figure 2. Torresdale Water Treatment Plant

sedimentation basin is approximately 15 to 20 hours (capacity: 176 MG).

Following initial settling, the raw water is pumped from the sedimentation reservoir to the rapid mix facilities. Three chemicals are 'routinely' applied to the water at this point: ferric chloride (as a coagulant), lime (for pH adjustment), and chlorine (for disinfection). Ferric chloride is normally added at a rate of 110 #/MG. Chlorine is added to breakpoint only at this point. pH is maintained at approximately 8.5. Occassionally, when taste and odor problems exist, powdered activated carbon (PAC) is also added at the rapid mix.

The flocculation chambers have a nominal detention time of 47 minutes. Slow mixer paddles are placed transversely to the direction of flow, providing a barrel-roll motion to the coagulated water. Following flocculation, the water flows through rectangular sedimentation basins with a theoretical detention time of 3.4 hours. Sludge is removed from the sedimentation basins continuously with mechanical rakes. Overflow weirs collect the coagulated and settled water where it begins its passage, by gravity, to the rapid sand filters.

Following sedimentation, but prior to filtration, the process stream is

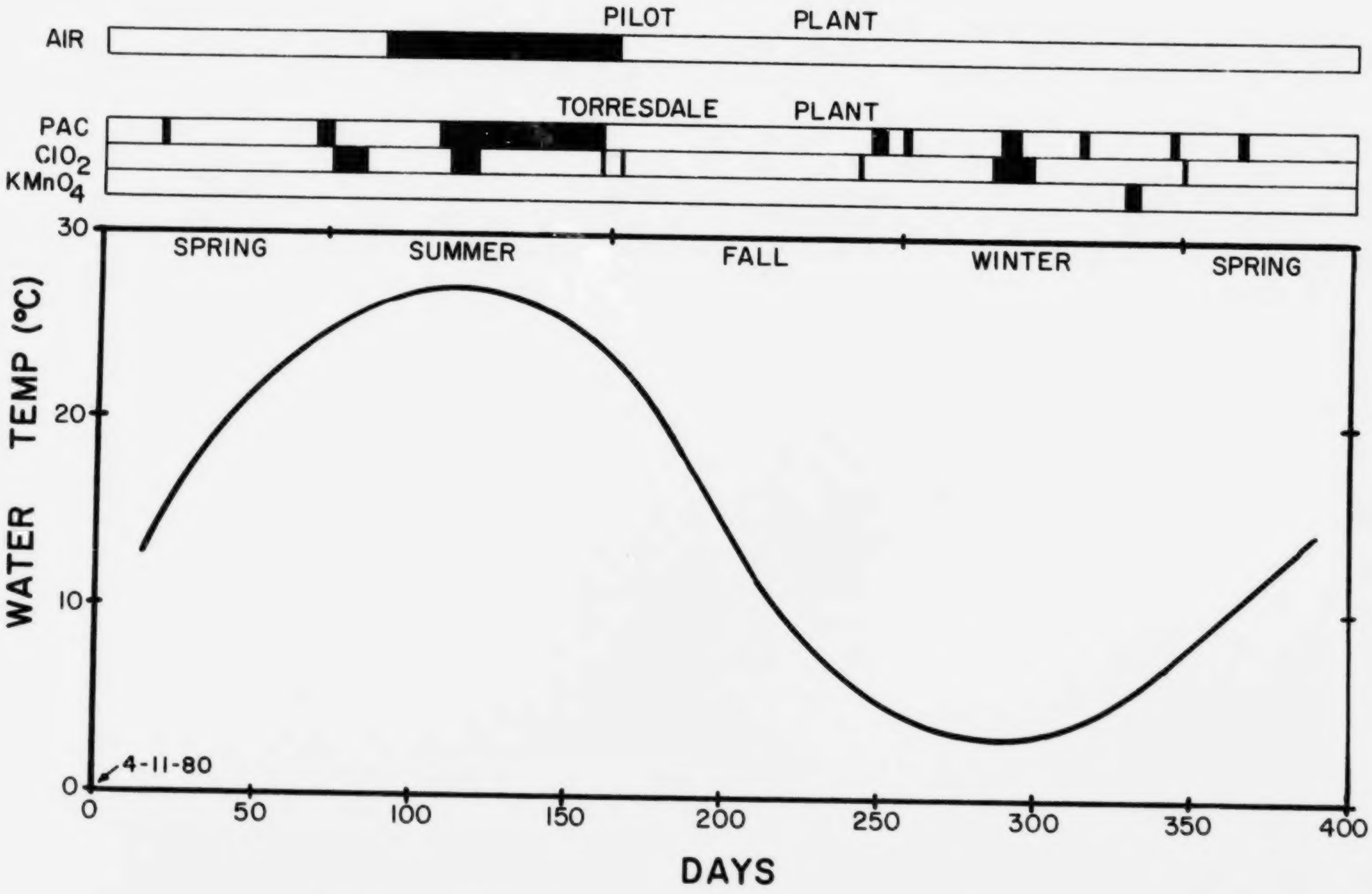


Figure 3. Water temperature variation of the Delaware River.

again disinfected. This is typically accomplished with a chlorine dose of approximately 2 mg/l. Since the breakpoint demand has already been satisfied, most of this chlorine dose goes directly to free chlorine.

The Torresdale Plant has 94 rapid sand filters each with 1041 square feet surface area. With the surface loading rate set at 2 gpm/sq. ft., the filter capacity is 282 MGD. The filters are equipped with Leopold bottoms and contain 10 inches of graded gravel and 28 inches of filter sand. Backwashing, although manually initiated, is automatically cycled. The backwash rate averages about 18.6 gpm/sq. ft.

It is at this point in the treatment process that the water used in the chlorinated AWT systems is drawn. It is necessary to specifically pump the water from the clearwell of the Torresdale Plant rather than draw water from a pressurized tap in the distribution system due to the post chemical addition of ammonia. Unlike free chlorine, the chloramines are not easily removed by the granular activated carbon.

Pilot Plant Description--

The Pilot Plant (Figure 4) draws its water from the Delaware River, just a few feet away from the intake gates of the Torresdale Water Treatment Plant. A submersible pump (Goulds Pumps, Seneca Falls, N.Y.) is used to continuously pump approximately 40 gpm from the river to a raw water sedimentation basin located 3000 feet from the intake. To protect the pump from any floating or suspended objects in the river, a 2 x 2 x 8 foot shaft is used. The shaft is constructed of cast iron sheeting and coarse stainless steel screening.

The raw water basin (RWB) has a capacity of 14,000 gallons, which allows for a detention of 12 hours time at the design flow rate of 20 gpm. An important feature of the RWB is that it is covered with a wood roof. This roof prevents excessive algae growth in the undisinfected water. Additionally, an overflow piping system is used to relieve the basin of excess flow from the river pump. To protect the Pilot Plant system from unexpected river pump breakdowns, the RWB is also equipped with an electronic level sensing device.

A centrifugal pump (Pacific Pumping Co. Oakland, Cal.) of 40 GPM capacity is used to draw the settled water through a 5 foot launder pipe in the RWB and deliver it 300 feet away to the Torresdale Plant filter building, where the Pilot Plant clarifier and filters are housed. The incoming raw water flow to the plant is then checked with a magnetic flowmeter and, if necessary, is adjusted manually. Typical flow rates for the pilot plant ranged between 10-20 gpm.

Following the flow meter the coagulant, ferric chloride, is added with a peristaltic pump at a dosage of 15 to 21 mg/l (125 to 175 #/MG). Also added at this location is a chemical for pH adjustment. At the start of the project, a 5% milk of lime solution was used. Difficulties in maintaining a sediment-free lime system, however, required a change in chemicals to sodium hydroxide. The sodium hydroxide was added with a positive displacement pump at a concentration of 75 mg/l; Pilot Plant pH was maintained at 8.0 - 8.5. During periods of low dissolved oxygen concentration, air was also injected into the water at this location (see Figure 3). Following these chemical

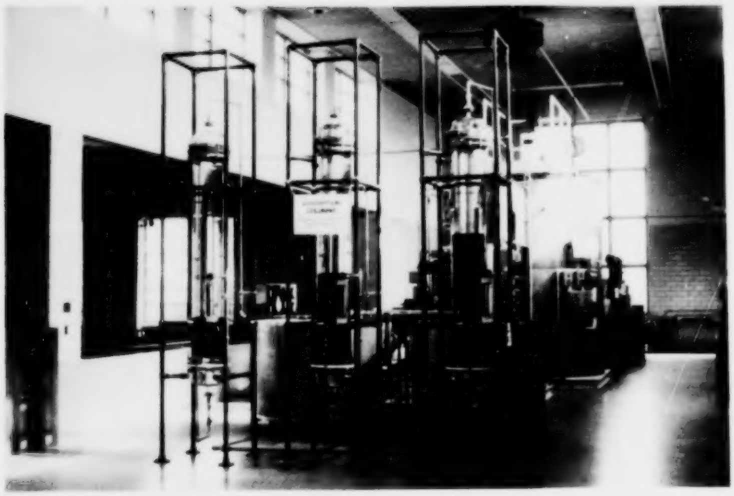


Figure 4. Pilot Plant

application points, only inert materials such as stainless steel, teflon, and glass came in contact with the process water.

The clarifier (General Filter Co., Ames, Iowa) is an upflow, solids contact unit made of 316 stainless steel which measures 8 ft. in diameter by 11 ft. 3 in. in height (Figure 5). It has a 3,600 gallon capacity, and a detention time of between three and six hours at the 10-20 gpm flowrate used during the study. The clarifier is equipped with nine sampling taps at various depths, sludge recycle, automatic sludge blowdown and liquid level control capabilities. With these controls, a sludge blanket of three to five feet deep was maintained. Clarifier overflow was collected by a two inch stainless steel peripheral launderer pipe.

Two rapid sand filters (RSFs) each with a five sq. ft. filter surface area (General Filter Co., Ames, Iowa) follow the clarifier (Figure 6). Each filter is 2 x 2.5 x 10 ft. and is constructed of stainless steel with a glass observation window. The filter media consists of 8 inches of graded gravel and 30 inches of filter sand (0.4 - 0.5 mm diameter). The filters are equipped with sight tubes for manual head-loss readings. Except for the initiation of backwash (when six foot of headloss is observed), the backwash sequence is fully automated. Backwash water is stored in two, 400 gallon stainless steel tanks. Backwash water is pumped at a rate of 75 gpm (15 gpm/ft^2), by a centrifugal pump (Aurora Pump, NE Aurora, Ill.), from the backwash tanks to the filters.

Following the rapid sand filters, the pilot plant effluent water is stored in the backwash water reservoir. This is the source of water for the nonchlorinated AWT systems.

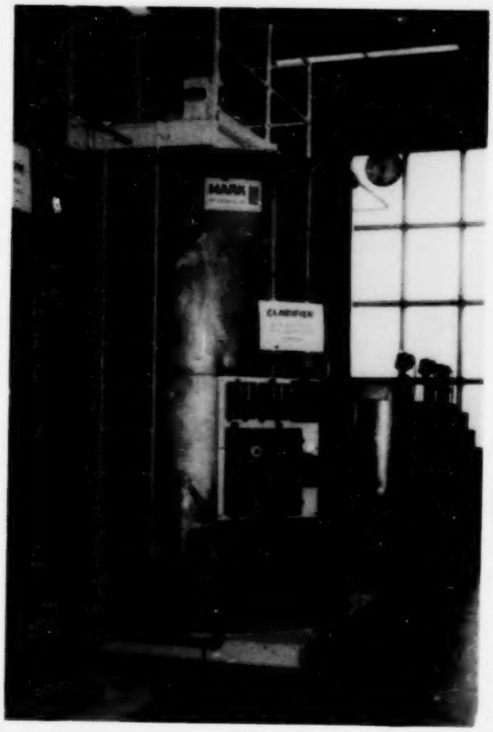


Figure 5. Pilot Plant Clarifier

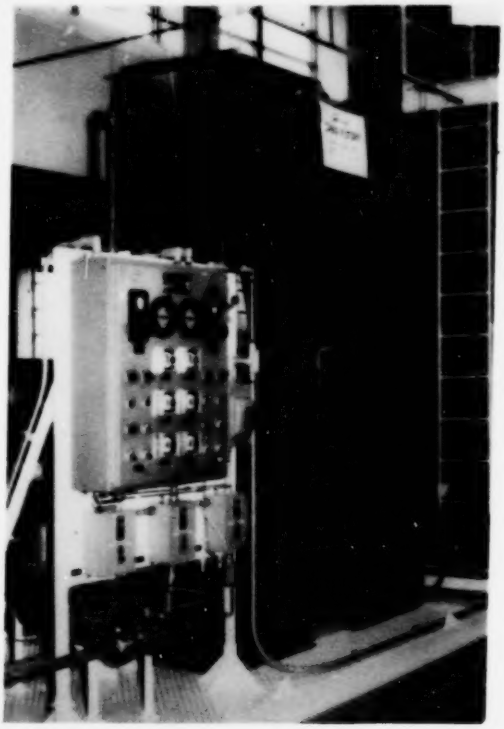


Figure 6. Pilot Plant Rapid Sand Filters

Advanced Water Treatment Systems

Following conventional treatment, the rapid sand filter effluents of the Torresdale and Pilot Plants are applied to the ozone and carbon contactors. Figure 7 is a schematic of the two conventional treatment trains and their respective AWT systems. The numbering system outlined in Figure 7 represents sampling sites. Table 4 describes those sampling sites relevant to the results to be presented in this report.

Ozonation Systems--

A schematic of the ozonation system used in the pilot scale investigations is presented in Figure 8. Ozone gas is generated on site with two ozone generators (PCI Ozone Corp., W. Caldwell, N.J.). Each unit is capable of generating 40 grams/hour (2 lbs/day) of ozone from dry air. Typically, however, the generators were operated well below capacity, at a flow rate of 2 scfm and an ozone concentration of only 1.0-1.5 mg/l (3-5 grams/hour). As an oxygen source for the ozone generators, ambient air is drawn through two compressors (Gast Corp., Benton Harbor, Mich.) and dried to a dew point of -40°F with heatless regenerative driers (General Cable Corp., Westminister, CO.).

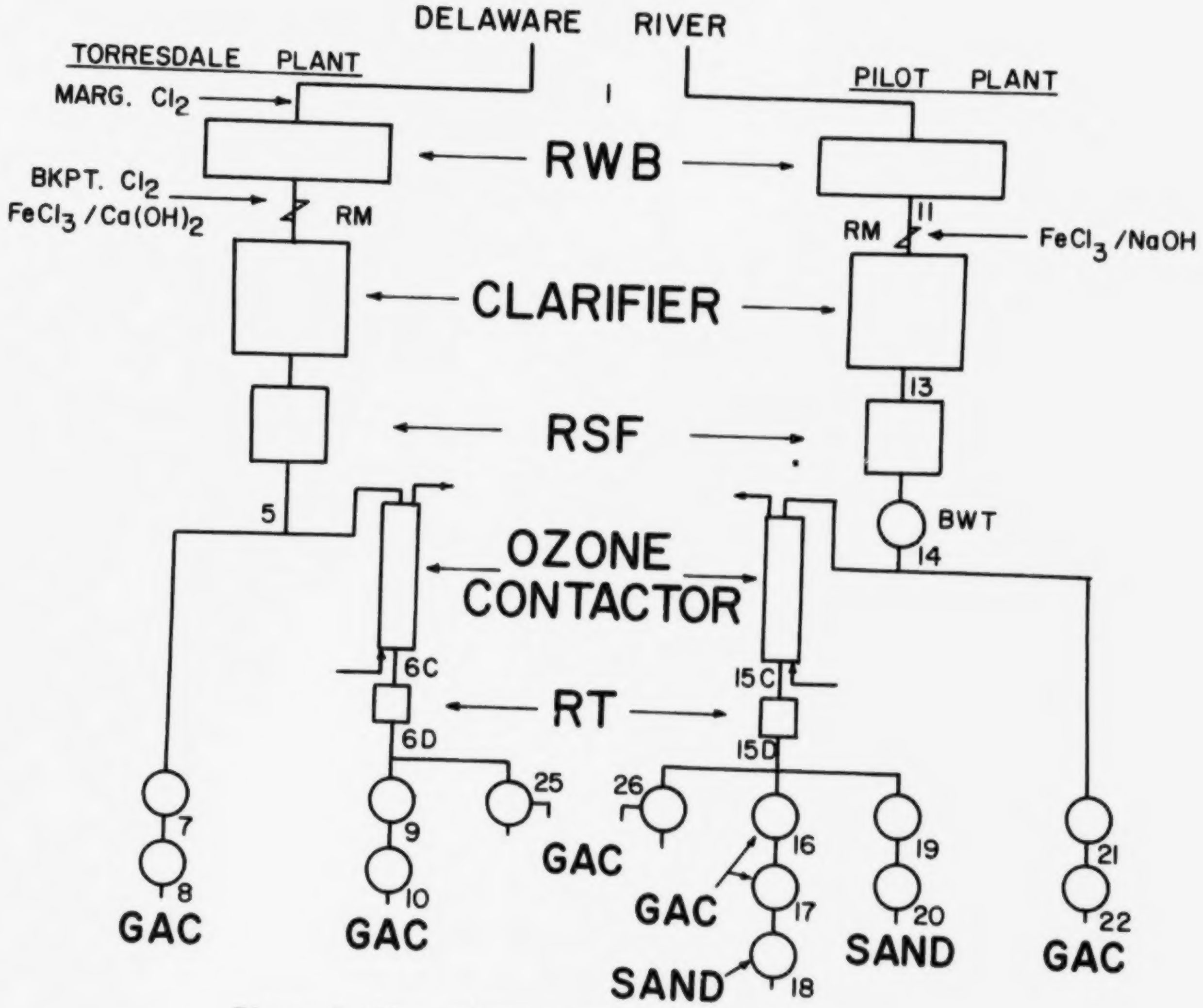

DELAWARE RIVER
TORRESDALE PLANT
PILOT PLANT
1
MARG. Cl_2
BKPT. Cl_2
$FeCl_3$ / $Ca(OH)_2$
RM
RWB
11
RM
$FeCl_3$ / NaOH
CLARIFIER
13
RSF
5
BWT
14
OZONE
CONTACTOR
6C
6D
RT
15C
15D
7
8
GAC
9
10
GAC
25
26
GAC
16
17
GAC
18
SAND
19
20
SAND
21
22
GAC

Figure 7. Flow schematic of pilot-scale studies.

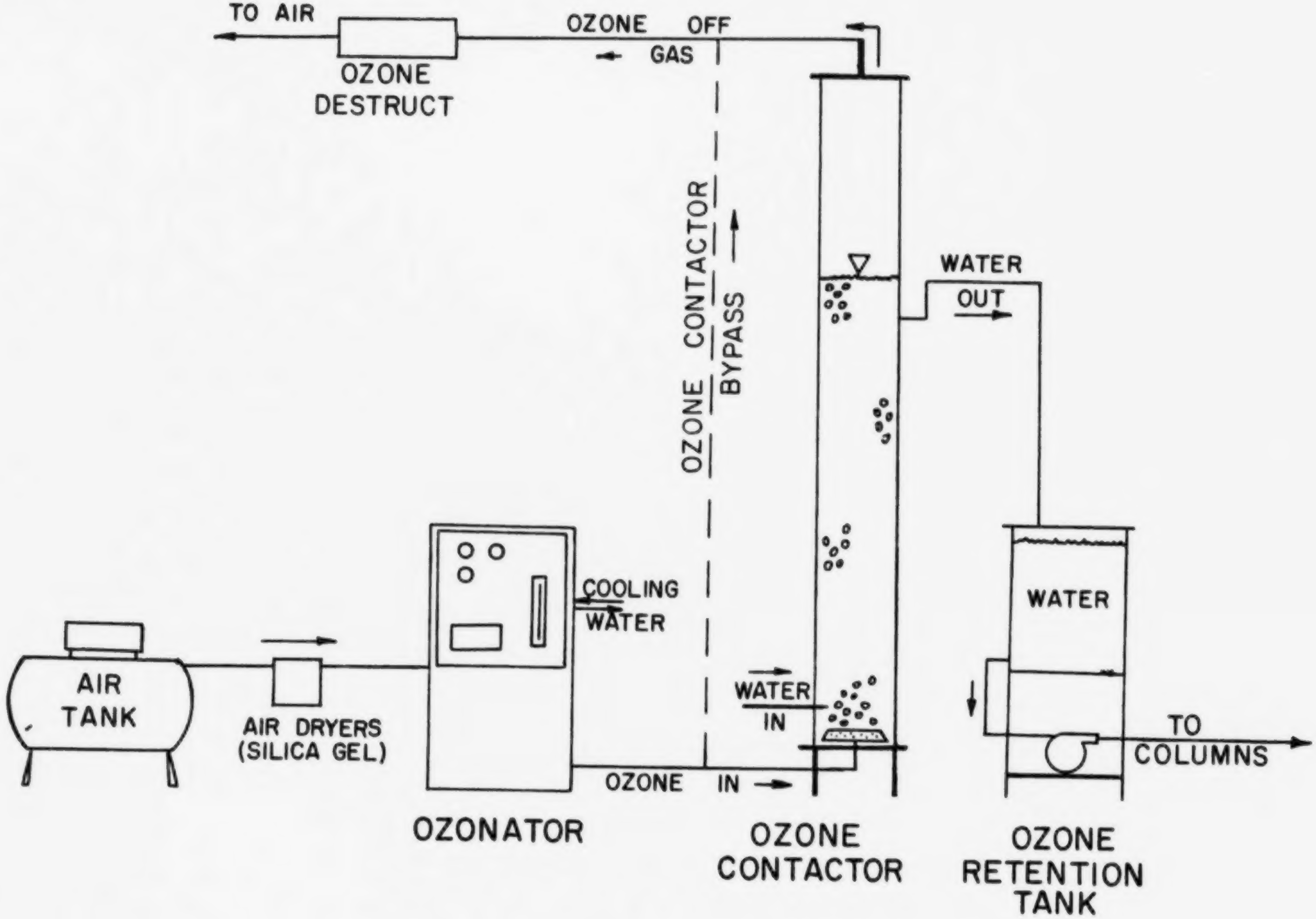

TO AIR
OZONE DESTRUCT
OZONE OFF GAS
OZONE CONTACTOR BYPASS
WATER OUT
AIR TANK
AIR DRYERS (SILICA GEL)
COOLING WATER
WATER IN
OZONE IN
WATER
TO COLUMNS
OZONATOR
OZONE CONTACTOR
OZONE RETENTION TANK

Figure 8. Ozonation System

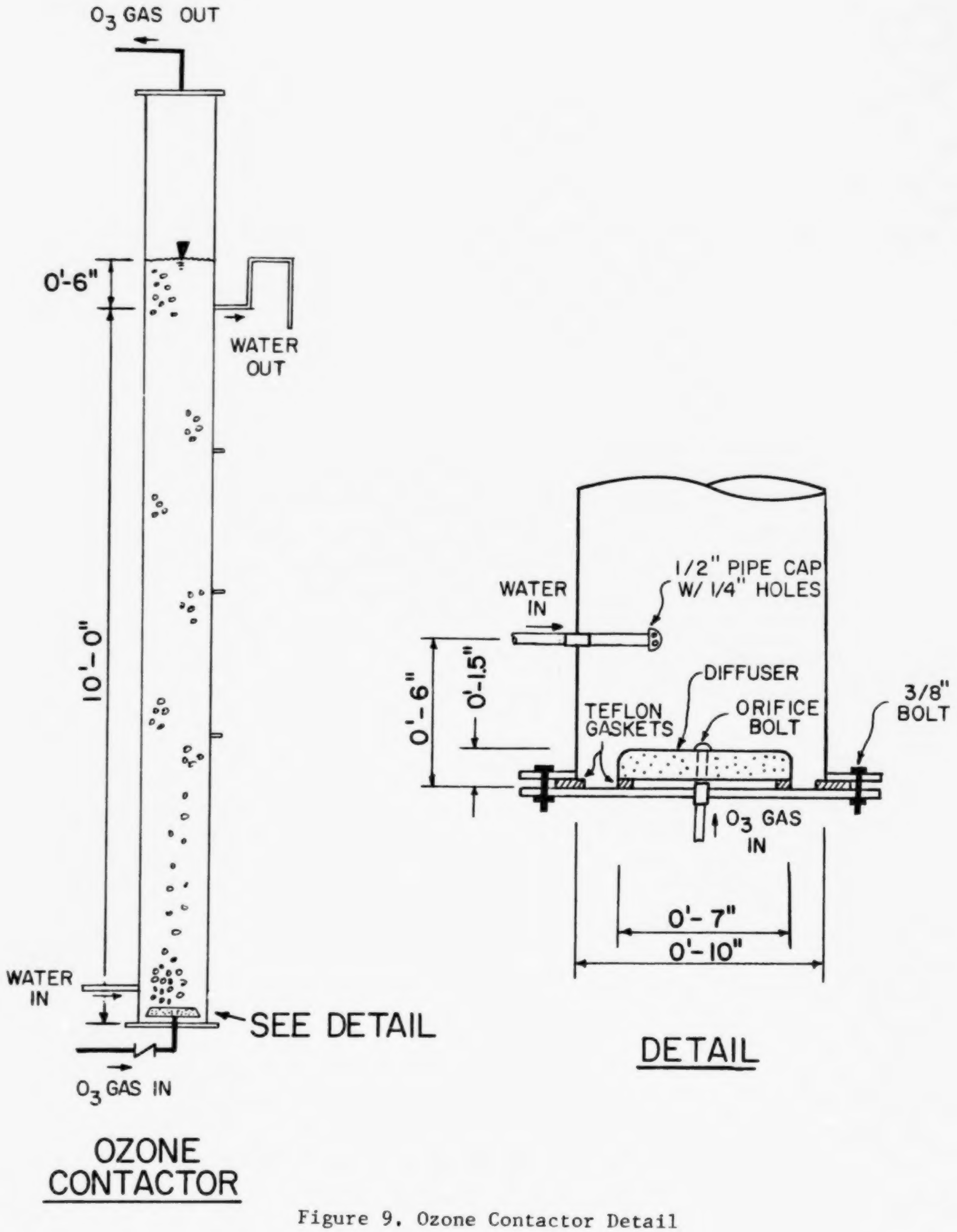
TABLE 4. SAMPLING LOCATIONS FOR PILOT STUDY

SITE NUMBERS (TP)	(PP)	SITE DESCRIPTION	NMEMONIC
1	11	Delaware River Water	RIVER
4	13	Clarifier Effluent	CLAR
5	14	Rapid Sand Filter Effluent	RSF
6C	15C	Ozone Contactor Effluent	O_3C
6D	15D	Ozone Retention Tank Effluent	O_3RT
7	21	GAC (15 Minute EBCT)	GAC_{15}
8	22	GAC (30 Minute EBCT)	GAC_{30}
9	16	Ozone/GAC (15 Minute EBCT)	O_3/GAC_{15}
10	17	Ozone/GAC (30 Minute EBCT)	O_3/GAC_{30}
-	19	Ozone/Sand (15 Minute EBCT)	$O_3/Sand_{15}$
-	20	Ozone/Sand (30 Minute EBCT)	$O_3/Sand_{30}$
25A	26A	Ozone/GAC (Multi-Tap) (7.5 Min EBCT)	$MT_{7.5}$
25B	26B	Ozone/GAC (Multi-Tap) (15 Min EBCT)	MT_{15}

(TP) = Torresdale Plant
(PP) = Pilot Plant

Stainless steel piping and teflon tubing directed the ozone gas flow from the generators to the contactors. The contactors were constructed of 316L stainless steel pipe measuring 13 feet in height and with an inside diameter of 10 inches. Figure 9 offers a profile view of the contactor. Table 5 presents typical operating characteristics for the two ozone contacting systems. To the extent possible, the contacting systems were operated under identical conditions.

Both ozone systems utilized co-current flow, where both the ozone gas and water enter the contactors from the bottom. For the diffusion of the ozone gas into water, a porous dome diffuser was used. These diffusers measured 7 inches in diameter and were made of ceramically bonded resins of aluminum oxide. Effective bubble size for the diffusers was rated at 0.2 mm. A polyvinyl chloride (PVC) bolt was employed as both the gas inlet and the diffuser fastener (see Figure 9, inset). Unfortunately, these bolts were found to be sheared in half and were therefore not properly securing the diffusers to the bottom support plates of the contactors. This is the apparent cause for the low ozone transfer efficiencies of the two systems (see Table 5). Fortunately, the identical situation was observed for both contactors, which allowed us to continue our comparison of the two systems. The resulting low ozone transfer efficiency was countered through long ozone/water contact times and high gas/water ratios. Thus the desired oxidation reactions were achieved at higher operating costs than would normally be necessary. As such, the cost analysis section of this report uses the organics results achieved in this study, but employs more standard values for ozone flow rate and contact time.


O_3 GAS OUT
0'-6"
WATER OUT
10'-0"
WATER IN
SEE DETAIL
O_3 GAS IN
WATER IN
1/2" PIPE CAP W/ 1/4" HOLES
0'-6"
0'-1.5"
DIFFUSER
TEFLON GASKETS
ORIFICE BOLT
3/8" BOLT
O_3 GAS IN
0'-7"
0'-10"

OZONE CONTACTOR

DETAIL

Figure 9. Ozone Contactor Detail

TABLE 5. OZONATION SYSTEM OPERATING PARAMETERS

Contactor	Torresdale Plant	Pilot Plant
Type	Co-Current	Same
Overall	13' x 10" Diam.	Same
Material	Type 316L S.S.	Same
Diffuser	7" Diameter (Ceramic Glass)	Same
Contact Time (Mins)		
O_3 Contactor	22	Same
O_3 Retention Tank	25	Same
Flow Rates		
Gas (SCFH)	65	77
Water (GPM)	2.0	2.0
G:W Ratio	4.1	4.8
Average Ozone Concentrations		
Applied Dose (mg/l)	1.2	1.2
O_3C Residual In Water (mg/l)	0.3	0.3
O_3RT Residual In Water (mg/l)	0.0	0.0
Ozone Utilized* (mg/l)	1.2	1.6
Ozone Transfer Efficiency (%)	25	17

*Ozone Utilized = $(G:W)\ ([O_3]_{G_{in}} - [O_3]_{G_{out}}) - [O_3]_{W_{out}}$

Following ozonation, the water is passed through stainless steel retention tanks which allow sufficient contact time to decrease the ozone residual in the water to below detectable limits. This maximizes the ozone/water contact time and minimizes the oxidation of the carbon granules. Centrifugal pumps transfer the water from the retention tanks to the O_3/GAC and the O_3/SAND systems.

Adsorption Systems--

Listed below are the four adsorption systems investigated in this study and a brief description of each:

TABLE 6. PILOT COLUMN DESIGN

	$GAC_{15,30}$	$O_3/GAC_{15,30}$	$MT_{7.5,15}$	$O_3/SAND_{15,30}$
Construction	Glass	Glass	Teflon	Glass
Diameter (inches)	6	6	1.6	6
Bed Depth (feet)	4, 8	4, 8	1.5, 3	4, 8
Media	Carbon*	Carbon*	Carbon*	Sand
Pre-Ozonation	No	Yes	Yes	Yes
SLR (GPM/Ft^2)	2	2	1.5	2
EBCT (Min)	15, 30	15, 30	7.5, 15	15, 30

*Calgon F-400 granular activated carbon

GAC(TP):	Chlorinated rapid sand filter effluent of the Torresdale Plant (Site 5) is applied to two GAC columns in series (Sites 7 and 8, respectively). EBCT=15 minutes each.
O_3/GAC(TP):	Chlorinated rapid sand filter effluent of the Torresdale Plant (Site 5) is ozonated (Site 6D) and applied to two GAC columns in series (Sites 9 and 10, respectively). EBCT=15 minutes each.
GAC(PP):	Non-Chlorinated rapid sand filter effluent of the Pilot Plant (Site 14) is applied to two GAC columns in series (Sites 21 and 22, respectively). EBCT=15 minutes each.
O_3/GAC(PP):	Non-chlorinated rapid sand filter effluent of the Pilot Plant (Site 14) is ozonated (Site 15D) and applied to two GAC columns in series (Sites 16 and 17, respectively). EBCT=15 minutes each.

Table 6 lists the design and flow characteristics of the GAC and O_3/GAC systems. A picture of a typical carbon system is shown in Figure 10. Each system consists of two columns operated in series. Each column is 6 foot in length with a 6 inch inside diameter. The columns are connected with teflon and stainless steel tubing. Each column has a 4 foot carbon bed depth and an EBCT of 15 minutes.

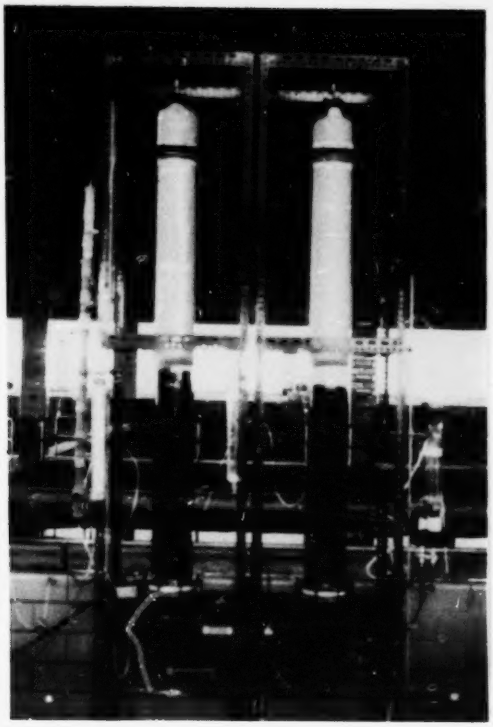


Figure 10. Carbon Bed Columns

All of the systems were operated under a pressure of approximately 15 psi. This allowed for the headloss to build up to 10-15 feet of water before backwashing was initiated. The backwashing process, which was operated manually, was performed on all columns at the same time.

All of the adsorption systems began operation on April 11, 1980. The study continued for 12 months at which time all of the columns were removed from service with the exception of the GAC_{15}(PP) and O_3/GAC_{15}(PP) systems, which remained in service for an additional 6 1/2 months.

In addition to the adsorption systems listed above, two 'mini-scale' multi-tap systems were also operated in the O_3/GAC mode. A description of these two systems is also given in Table 6. The columns, constructed of 1.6 inch diameter teflon segments of approximately 5 inch length (Savillex Corporation, Minnetonka, Minn.) each has a sampling port which allows for the collection of both water and GAC samples. These systems were used to determine bacterial concentrations at various depths through the bed.

O_3/SAND System--

In addition to the adsorption systems, an O_3/SAND system was also investigated. This system was operated in parallel to the O_3/GAC (PP) system. A description of this system may be summarized as:

O_3/SAND (PP): Non-chlorinated rapid sand filter effluent of the Pilot Plant (Site 14) is ozonated (Site 15D) and applied to two sand columns in series (Sites 19 and 20, repectively). EBCT=15 minutes each.

The design and flow characteristics of the O_3/SAND system are listed in Table 6. The only difference between this system and the O_3/GAC(PP) system is the sand media in the O_3/SAND system. Any organic removal observed through the O_3/SAND system is due to either oxidation, volatilization or biodegradation, since no adsorption will take place in the O_3/SAND system. Knowing the extent of each of the above then becomes a useful tool in determining the relative importance of biodegradation and adsorption in the carbon beds of the O_3/GAC(PP) system.

O_3/SAND Studies--

A six month investigation of the O_3/SAND System was initiated one year following the start-up of the O_3/GAC pilot studies. The primary purpose of the O_3/SAND investigation was to determine whether any significant increases in organic mineralization and/or biodegradability could be achieved through changes in the operating parameters of the Pilot Plant ozone contactor. A total of five studies were conducted. The operating parameters investigated were: applied ozone dosage, ozone/water contact time, and direction of water flow through the contactor.

A general flow schematic for the five studies is shown in Figure 11. A description of the sites shown is listed in Table 7. In each study, one O_3/SAND system was used for control purposes (the Control System), while the other system underwent process changes (the Experimental System). The unchlorinated effluent of the Pilot Plant rapid sand filter (Site 14) served as the influent to both ozone contactors. Following ozonation, the ozone retention tank effluents (Sites 15D and 29D), were applied to sand beds (Sites 32 and 36). Each sand bed had an EBCT of 15 minutes. This contact time was found sufficient for the bacteria on the sand beds to remove any biodegradable organics from the process stream. An additional sand bed (Site 34) received nonozonated Pilot Plant rapid sand filter effluent (Site 14). It was operated as a control system in order to determine whether any biodegradable organics were in the water applied to the ozone contactors. At each sampling location DOC, A254 and THMFP samples were collected. In addition, both the halogenated and nonhalogenated volatile organic compounds measured during the pilot study were also tested.

A summary of the operating conditions for the O_3/SAND Studies is shown in Table 8. The objective of the first O_3/SAND study, The Ozone Contactor Performance Comparison, was to determine whether the two ozone systems would yield equivalent results when operated under identical conditions. This

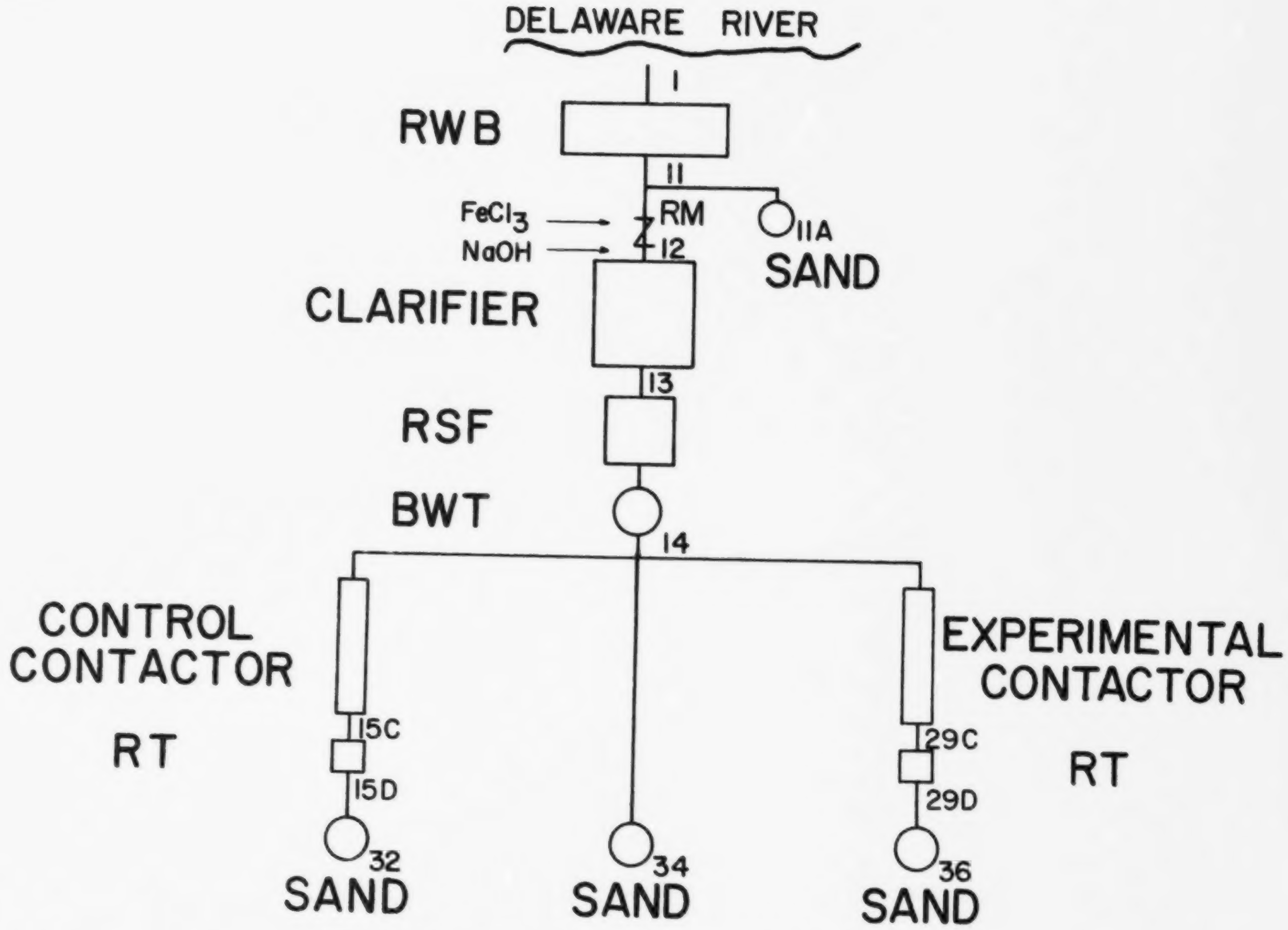

DELAWARE RIVER
1
RWB
11
FeCl$_3$
NaOH
RM
12
11A
SAND
CLARIFIER
13
RSF
BWT
14
CONTROL CONTACTOR
RT
15C
15D
32
SAND
34
SAND
EXPERIMENTAL CONTACTOR
RT
29C
29D
36
SAND

Figure 11. Flow schematic of ozone/sand studies.

TABLE 7. SAMPLING LOCATIONS FOR O_3/SAND STUDIES

Site Numbers		Site Description	Nmemonic
Control System	Experimental System		
14	14	Rapid Sand Filter Effluent	RSF
15C	29C	Ozone Contactor Effluent	O_3C
15D	29D	Ozone Retention Tank Effluent	O_3RT
32	36	Ozone/Sand (15 minute EBCT)	$O_3/Sand_{15}$
34		Sand (15 minute EBCT)	$Sand_{15}$

study was crucial not only as a prelude to the other O_3/SAND studies, but also as a check on the comparability of the results obtained from the two contactors during the O_3/GAC run.

The objective of the second study was to determine the influence of ozone/water contact time on the reduction of organic compounds from the process stream. This was accomplished by doubling the contact time in the experimental contactor.

In the third study both the ozone dosage and the ozone/water contact time in the experimental system were doubled. Due to the relatively high levels of DOC removal observed during this investigation, a fourth study was undertaken to look at the effects of increased ozone dose alone.

The objectives of the last study were to determine whether the relatively poor ozone transfer efficiency of the ozone contactor could be improved through a redirection of the water flow through the contactor. The control system was kept as a co-current flow contactor while the experimental system was converted to a counter-current system.

MINI COLUMNS

The overall purpose of this mini column study was to determine the mechanisms of long term TOC removal in a GAC contactor. An understanding of the mechanisms of organic removal in an adsorptive system is essential to developing predictive mathematical models and optimizing the adsorptive unit process for potable water treatment.

The overall purpose was accomplished through a series of experiments designed to separate the effects of adsorption and biodegradation in a GAC contactor. The major points addressed in the experiments were:

1. The relative contributions of bacterial degradation and slow adsorption to TOC removal in a GAC contactor.

TABLE 8. OPERATING CONDITIONS FOR O_3/SAND STUDIES

Study	CONTROL OZONATOR			EXPERIMENTAL OZONATOR		
	O_3Dosage (mg/l)	Contact Time (Min)	G:L*	O_3Dosage (mg/l)	Contact Time (Min)	G:L*
1)Ozone Contactor Performance Comparison	1.2	22	4.6	1.2	22	4.4
2)Contact Time Comparison	1.5	22	4.6	1.5	44	9.2
3)Contact Time & Ozone Dosage Comparison	2.1	22	4.3	4.1	44	8.6
4)Ozone Dosage Comparison	2.2	22	4.6	4.0	22	4.1
5)Co-current Versus Counter-current Flow Comparison	2.0	22	4.7	2.0	22	4.7

*G:L - gas to liquid ratio.

2. The reproducibility of column adsorption studies for inorganic, organic, and microbial parameters.

3. The effect of temperature on the biological degradation and activated carbon adsorption from dilute concentrations of organics.

4. The use of sand as an alternate media for estimation of bioactivity in GAC contactors.

To accomplish the major goals of the study, an experimental approach was required to differentiate between adsorptive and biological TOC removal. The experimental approaches used in this study were:

1. The development of an experimental method to inhibit biological TOC removal on GAC without affecting adsorption.

2. The use of dissolved oxygen removal as an indirect measure of bioactivity in a GAC contactor.

The mini column work was conducted using effluent from the Pilot Plant ozone retention tank at the Torresdale Water Treatment Plant under field conditions (i.e. low and fluctuating organic concentrations with seasonal temperature variations). The parameter TOC was monitored for the following reasons:

1. Quasi steady state removal has been demonstrated for this parameter at Philadelphia and elsewhere (133) suggesting biodegration as the mechanism of removal.

2. Competition between specific organics and natural background organics as measured by TOC (24) or humic substances (111) has been demonstrated.

3. Humic materials act as precursors in the formation of THMs in potable water treatment (13, 134). Humic materials comprise up to 90% of the natural background organic load found in natural waters (9). THMs and TOC have been correlated in potable water (109), although this has not yet been demonstrated in a general fashion.

Several small scale experiments were conducted with the common focus of determining the mechanism of long term TOC removal and quantifying the bacterial contribution to the long term removal. The following section discusses in detail the concepts used to approach separating bacterial and adsorptive removal. Five specific experiments were conducted using small scale GAC contactors, as follows:

1)Oxygen Uptake on GAC- -

The purpose of this experiment was to determine whether chemical oxygen uptake by carbon in the presence of little or no bioactivity could be reduced to a negligible amount. This is important in determining the use of oxygen removal as an indirect measure of bioactivity.

2)Adsorption Reproducibility- -

The purpose of this experiment was to demonstrate that column studies were reproducible under the experimental setup utilized herein. This gives a baseline of error from which to draw conclusions about the significance of data from parallel contactors and demonstrates the negligible effects of temperature on the adsorption mechanism of TOC removal in a GAC contactor. Demonstrating negligible effects of temperature on adsorption in the GAC contactors used in this study becomes important later when comparing biological and adsorptive TOC removals.

3)Long Term TOC Removal- -

The purpose of this experiment was to demonstrate that TOC removal could be controlled by temperature once the adsorptive capacity had been exceeded. It also allows comparison with other GAC experiments as reviewed by Roberts and Summers (133) in terms of the characteristics of the Philadelphia project with respect to projects elsewhere in the world.

4)Bacterial Growth Characteristics- -

The purpose of this experiment was to determine specific growth rates of bacteria on GAC contactors. This allows comparison of the GAC system with other microbiological ecosystems with regard to the level of activity and potential for activity.

5)TOC Removal Rate- -

The purpose of this experiment was to determine the rate of biological TOC removal on sand as compared to GAC. This determines the applicability of sand as an estimator of bioactivity on GAC. Once the rates of removal on sand and GAC are demonstrated to be comparable, the relative contributions of biodegradation and slow adsorption can be determined.

Mini Column Construction

The contactors were constructed of segmented Teflon units with side ports for removing carbon without taking the contactor out of service. The Teflon segments (Savillex Corporation, Minnetonka, MN, part #504-25) were 4.75 inches high with an inside diameter of approximately 1.6 inches. Eight segments were coupled (part #502) together for an overall height of approximately 40 inches. Stainless steel screen was cut to fit the end caps (part #551-25) of the contactors. This was installed to prevent carbon and sand from washing out of the contactor. Table 9 summarizes the bench scale contactor characteristics.

Sampling valves were installed at the lowermost port of the bench scale contactors. Sampling valves (Penn Valve and Fitting, Willow Grove, PA, part #SS-4MG) were connected to 0.25 inch stainless steel tube, which was inserted into the port. Small holes drilled into the stainless steel were used to insure collection of a sample from the center of the contactor. Sand was placed in the contactor from the sampling valve to the end cap (approximately 0.75 inches). The valves were used for sampling bacterial densities during the adsorption reproducibility experiment. Samples for all other parameters were collected at the column outlet. Figure 12 is an illustration of the bench scale contactors.

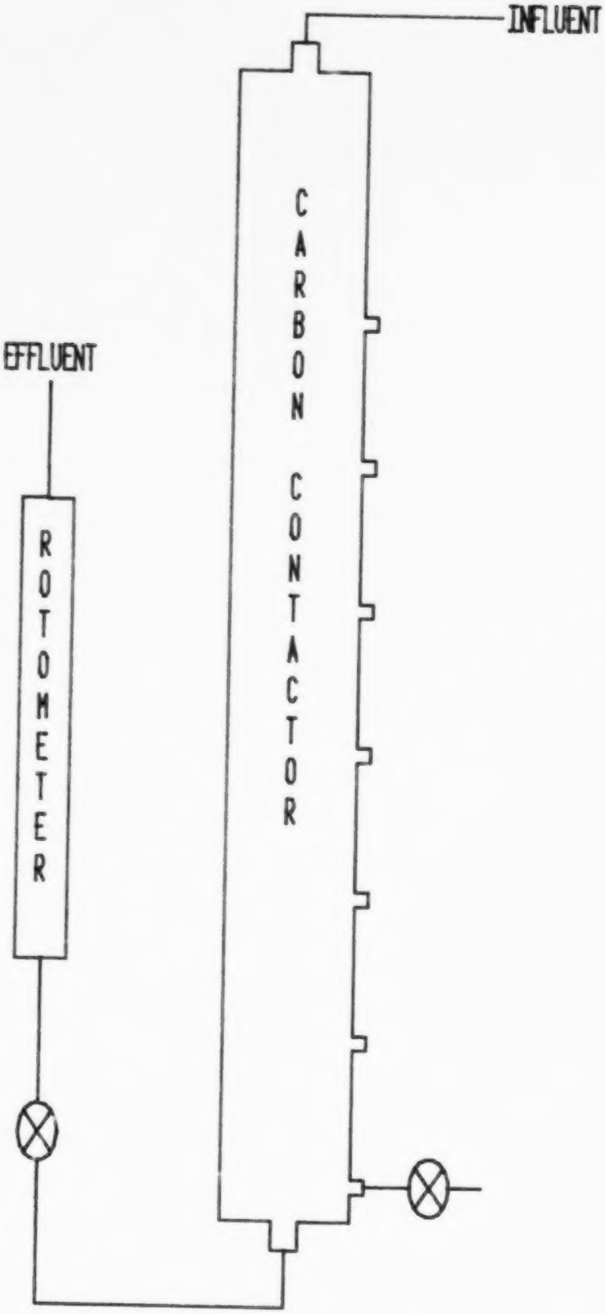

INFLUENT
EFFLUENT
ROTOMETER
CARBON CONTACTOR

Figure 12. Schematic of Teflon mini column

Table 10 describes how the bench scale contactors were utilized during the experiments. In all experiments except oxygen uptake, column flow was controlled by a multi-head Masterflex pump (Cole Parmer Corporation, Chicago, IL, pump = part #P-7545-10, head = part #P-701500, tubing = part #P-6411-45). The pumps were operated by variable speed drives which had a capacity range of approximately 20 to 170 ml/min. This ensured that each column would receive the same flow. Gilmont rotometers (Cole Parmer Corporation, Chicago, IL, part #C-3203-20, range = 3 to 290 ml/min) were used to measure flow on a day to day basis. These rotometers were calibrated at the onset of the study and checked several times after installation at the Torresdale pilot plant. During the course of the experiments, a temperature induced viscosity change caused the chilled rotometers to read high compared to the warm rotometers. However, calibration checks on the warm versus cold lines showed that the Masterflex pump was metering flow in all lines equally.

Water samples for all parameters (except bacterial density measurements during the adsorption reproducibility experiment) were collected by disconnecting the line between the rotometer and the pump. The flow was set using a regulating valve (Penn Valve and Fitting, Willow Grove, PA, part #SS-1RS4) on the 0.25 inch line from the contactor to the rotometer. The flow was set at the rotometer value read before the pump was disconnected, as the pump was more reliable than the rotometers when water of different temperature was being passed (as described above). Water pressure was supplied by a centrifugal pump located after the ozone retention tank. Once the flows had been set, the 0.25 inch line was removed from the rotometer inlet for sample collection. After collection, the line to the Masterflex pump was connected to the effluent port of the rotometer, the sample line was connected back to the influent port of the rotometer and the regulating valve was fully opened to allow flow regulation by the Masterflex pump only.

Table 11 lists the parameters and analytical methods used in this study by experiment number.

TABLE 9. BENCH CONTACTOR PHYSICAL CHARACTERISTICS

Inside Diameter - 1.6 inches
Nominal Wall Thickness - 0.125 inches
Length - 40 ± inches
Material - Teflon
Connection and Sampling Ports - 0.25 inch tube fitting
Connecting Lines - 0.25 inch teflon tube

TABLE 10. MINI COLUMN EXPERIMENTS

	Column Length (Inches)	Study Duration	# of Columns	Column Packing	Water Source
1. Oxygen Uptake on GAC	40 ±	17 days	4	GAC	Recycled Distilled
2. Adsorption Reproducibility	40 ±	77 days	2 to 8	GAC	Pilot Plant
3. Long Term TOC Removal	40 ±	539 days	2	GAC	Pilot Plant
4. Bacterial Growth	20 ±	66 days	2	GAC	Pilot Plant
5. TOC Removal Rate	40 ±	61 days	4	GAC, Sand	Pilot Plant

Table 11. MINI COLUMN EXPERIMENTAL PARAMETERS

Parameter	Experiment Number 1	2	3	4	5
Dissolved Oxygen	X	X	X		X
Total Organic Carbon		X	X		X
pH		X			
Alkalinity		X			
A254		X	X		
Carbon Dioxide Evolution		X			
Bacterial Density	X	X	X	X	X
Temperature		X	X		X

Table 12. MINI COLUMN OPERATING CHARACTERISTICS

Flow Rate	80 ml/min
EBCT*	15 minutes
Carbon Type	Calgon Filtrasorb 400
Carbon Depth	36 ± inches

* Empty Bed Contact Time

Oxygen Uptake on GAC

The purpose of this experiment was to determine if the dissolved oxygen removal could be lowered to a negligible amount by filtering out bacteria in Millipore filters (0.22 µm Durapore Cartridge #CVGL10P1). This would then determine whether DO removal could be used as an indirect measure of bioactivity on GAC filters. This experiment was also intended to provide a baseline of information on the operating characteristics of the small scale contactors. The interaction of dissolved oxygen and granular activated carbon has been studied extensively (123).

Figure 13 shows a schematic diagram of the experimental set up. Sampling points are marked with an asterisk(*). Distilled water was recycled by a positive displacement pump (Milton Roy, Ivyland, PA, Model #R251-144). Flow rates were controlled by regulating valves (Penn Valve and Fitting, Willow Grove, PA, part #SS-1RS4). Table 12 gives the operating characteristics for this and all experiments in this study.

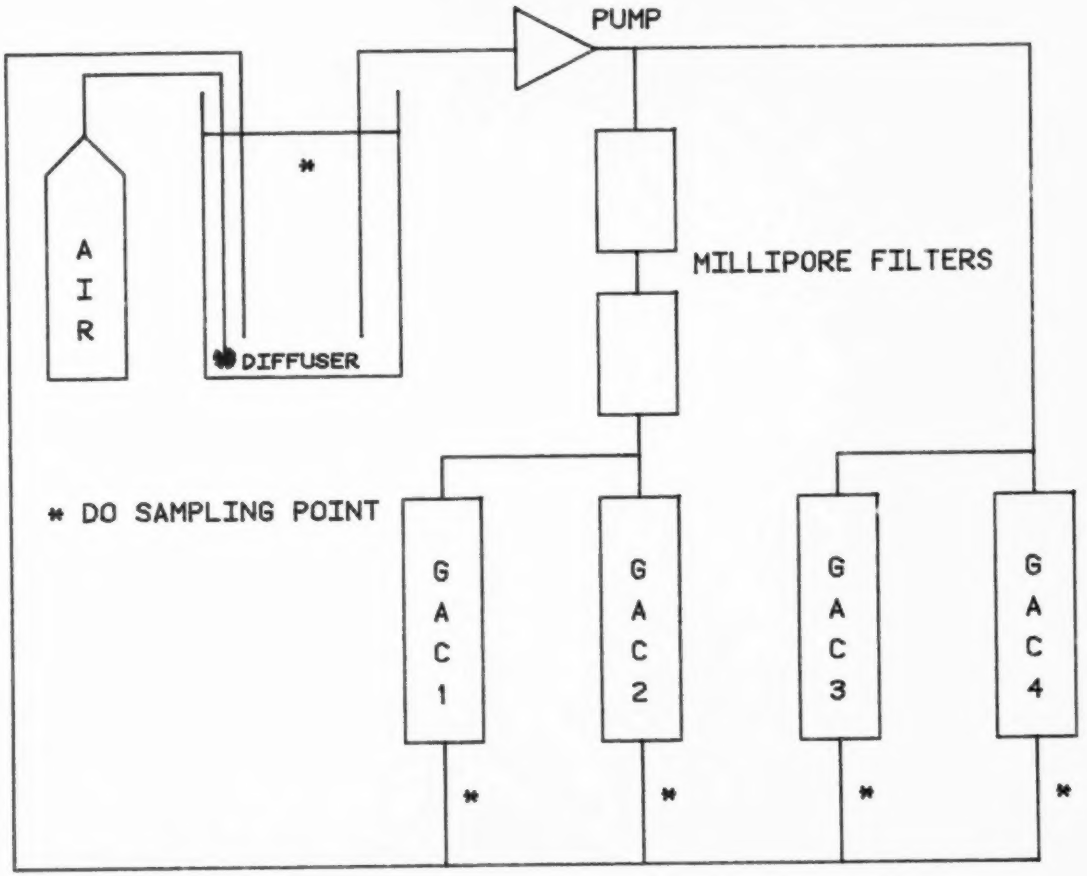

PUMP
MILLIPORE FILTERS
A I R
DIFFUSER
*
* DO SAMPLING POINT
G A C 1
G A C 2
G A C 3
G A C 4
*
*
*
*

Figure 13. Oxygen Uptake Schematic Diagram

Adsorption Reproducibility

The purpose of this experiment was to demonstrate that column studies were reproducible under the experimental setup utilized herein. This gives a baseline of error which must be exceeded prior to drawing conclusions about the significance of data from parallel contactors and measures whether or not the effects of temperature on the adsorption mechanism of TOC removal in a GAC contactor are negligible. Demonstrating negligible effects of temperature on adsorption in the GAC contactors used in this study becomes important later when comparing biological and adsorptive TOC removals. The effects of temperature on adsorption are of primary import to this study as it is the principle method which will be used to differentiate between adsorptive and biological TOC removal.

This experiment was the most detailed investigation undertaken in the mini column study. The operating characteristics are shown in Table 12. The object was to acclimate a set of contactors to the pilot plant water for a seven week period, then lower the temperature to some of the contactors for comparison to others which remained at ambient temperature. The seven week period would allow the bacterial populations to become stable, after which bacterial activity could be inhibited by the lower temperature of the cold contactor. Acclimation of bacterial populations at the ambient temperature for all contactors was done to avoid selecting for cold adapted bacteria.

The methods for differentiating between biological and adsorptive TOC removal allows the experiments to proceed under conditions normally encountered in potable water treatment. All contactors would be subject to seasonal temperature variations, but a temperature differential would be maintained without passing the range normally encountered at Philadelphia. The temperature dependency of most reactions has been found to be well represented by Arrhenius' Law (128):

$$k = k_o \exp(-E_a/RT)$$

where k = reaction rate at temperature T
E_a = activation energy
R = universal gas law constant
T = absolute temperature

The key to the rate of reaction is E_a, the activation energy. Physical mechanisms such as diffusion and adsorption have small activation energies, up to 5 kcal/mol-°K. These reactions show little temperature dependency. Previous work with activated carbon indicates that normal temperature variations have only minor effects on the adsorptive process (129).

A general rule of thumb for biological systems states that for a 10 degree (centigrade) increase in temperature, the reaction rate should double. This corresponds to an activation energy in the range of 10 to 20 kcal/mol-°K. Stephenson (130) measured the effect of temperature on *Escherichia coli* using various substrates and found an average ratio of 2 for the temperature range of 23 to 33 degrees centigrade in a growth limited system. In an (activated sludge) substrate limited system, the ratio of rates has been measured as low as 1.35 (131). In a study similar to the one presented herein (44), parallel GAC contactors operated at 5 and 25 degrees centigrade, treating wastewater treatment effluent, produced a differential TOC removal.

Assessing the contribution of bacteria to TOC removal in a GAC contactor requires knowledge of the rate constant for bacterial TOC removal. This was to be measured by removing sections from the GAC contactors and measuring carbon dioxide evolution in biometers and Warburg respirometers. For this reason, GAC contactors were taken offline once every two weeks and analysis of cores from the contactors was conducted. Samples of the carbon cores were placed in biometers and respirometers for measurement of oxygen uptake and carbon dioxide evolution. Core samples were also analyzed for bacterial density. Samples for dissolved oxygen, TOC, pH, alkalinity and A254 were taken from on line contactors once weekly for the first seven weeks (prior to dropping the temperature).

The temperature was dropped on two of the contactors after seven weeks. Figure 14 is a schematic diagram of the adsorption reproducibility experiment. After seven weeks, contactors 1 through 4 had been taken off line for analysis and only contactors 5 through 8 remained. The sampling frequency for TOC, DO, A254, and temperature was increased to once every two days. Contactors 5 and 6 were taken off line at week nine and core samples were analyzed as described above.The two remaining contactors were maintained for long term evaluation as described in the following section.

Long Term TOC Removal

The purpose of this experiment was to demonstrate that TOC removal could be controlled by temperature once the adsorptive capacity had been exceeded. It also allows comparison with other GAC experiments as reviewed by Roberts and Summers (133) in terms of the characteristics of long term TOC removal observed in the Philadelphia project with respect to projects elsewhere in the world.

The adsorption reproducibility experiment provided a baseline of data indicating that temperature could not induce a TOC removal differential in the short run, as was also shown by Maqsood and Benedek (44) for wastewater effluent. Therefore, contactors number 7 and 8 were maintained on line until a temperature induced TOC differential could be attained. The operating characteristics were maintained as shown in Table 12, however, changing seasons required modification of the operation of the temperature control. As winter approached, the operation was switched from ambient-chilled to warmed-ambient. In all, six operational modes were employed throughout the study. Table 13 gives the temperature range and duration of the various modes of operation. This table defines operating temperatures for bench scale experiments 2 through 5. Days 1 through 77 (Mode A and part of Mode B) represent the adsorption reproducibility experiment and days 479 to 539 (Mode F) represent the TOC removal rate experiment. The operational modes were changed in response to seasonal changes at the plant, aimed at maintaining the temperature differential, and do not correspond directly to the experiments.

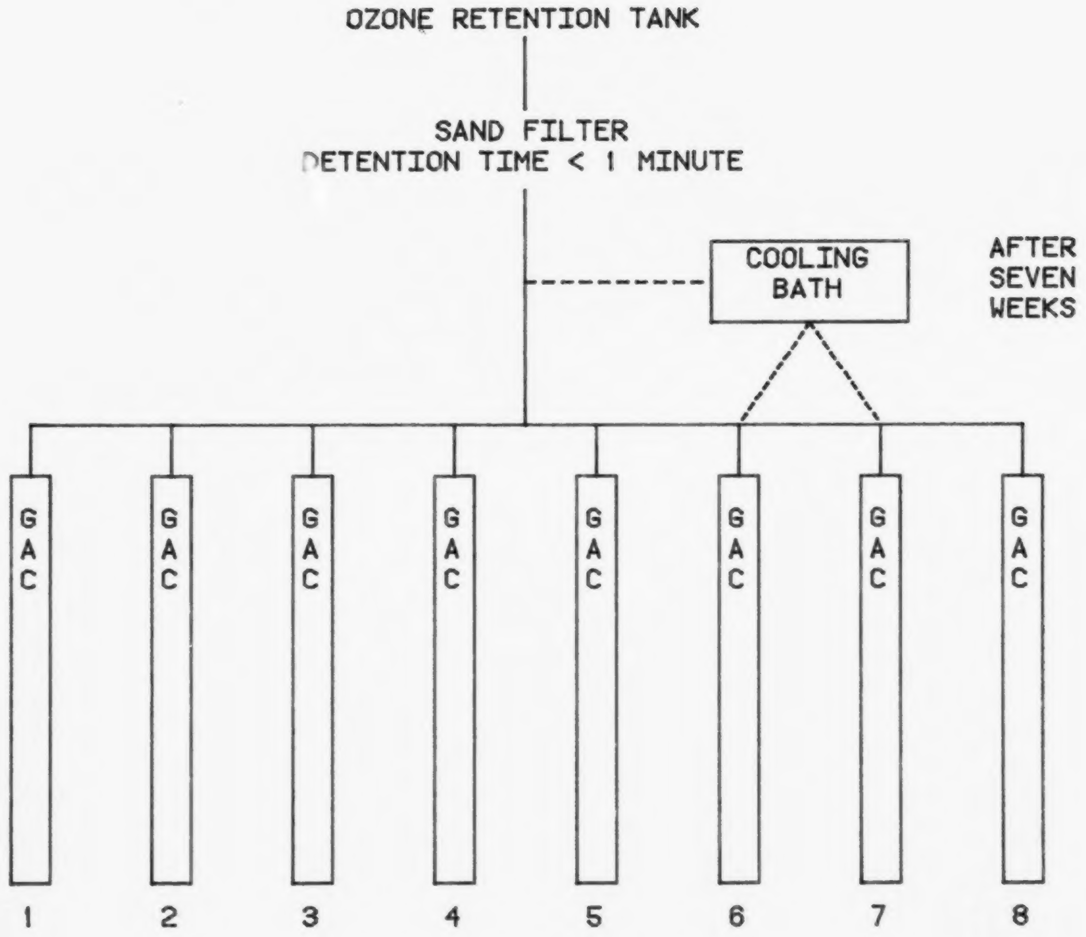

OZONE RETENTION TANK
SAND FILTER
DETENTION TIME < 1 MINUTE
COOLING BATH
AFTER SEVEN WEEKS
GAC
1
2
3
4
5
6
7
8

Figure 14. Adsorption Reproducibility Schematic Diagram

TABLE 13. BENCH SCALE CONTACTOR OPERATIONAL MODES

Mode	Dates of Operation	Days	Temperature Range (Degrees Centigrade) Contactor 7 (cold)	Temperature Range (Degrees Centigrade) Contactor 8 (warm)	Comments
A	06/02/80-07/23/80	1-52	24-30	24-30	Ambient
B	07/23/80-11/16/80	52-167	6-17	15-31	Chilled-Ambient
C	11/16/80-04/30/81	167-325	6-17	27-32	Ambient-Warmed
D	04/31/81-07/13/81	325-407	30-35	30-35	Warmed-Warmed
E	07/13/81-09/22/81	407-478	25-29	25-29	Ambient
F	09/22/81-11/23/81	478-539	5-15	16-23	Chilled-Ambient

Sampling was curtailed after the adsorption reproducibility experiment. The parameters pH, alkalinity, and carbon dioxide evolution by Warburg and biometer were discontinued. Alkalinity and pH measurements were dropped because no changes were seen in these parameters across a GAC contactor. Carbon dioxide evolution was dropped because contactors were no longer being taken off line for core analysis.

The long term TOC experiment served many purposes. It allowed refinement and testing of the experimental method developed here and noted in the following two paragraphs. It was run long enough to achieve a steady state removal as defined by Roberts and Summers (133) and showed the two distinct phases of adsorber performance as demonstrated by Maqsood and Benedek (44) in which the carbon acts first as an adsorbent and then as a support for biological growth as well as an adsorbent.

An important emphasis of the long term study was to observe and compare TOC and dissolved oxygen (DO) removal under various temperature conditions. The adsorption reproducibility experiment had demonstrated pronounced effects of temperature on DO removal without an accompanying TOC differential. Therefore, it was essential to determine to what extent DO removal was related to TOC removal. Previous workers (31, 135) have related TOC and DO removal, using the latter as an estimate and proof of bioactivity on GAC.

Another important emphasis was placed on determining to what extent TOC removal could be manipulated by temperature control. Data presented later will lead to two interpretations of mechanism for a temperature induced TOC differential. By changing the mode of operation, it was possible to determine whether temperature was controlling bioactivity only, or whether it could have a measurable effect on adsorption as well.

Bacteria Growth

Typical GAC investigations in the U.S. involved post treatment. In these situations, pre-chlorination had suppressed bacterial activity such that the influent bacterial densities were negligible compared to effluent densities. However, during the long term operation of the mini columns receiving non-chlorinated pilot plant water, bacterial densities in the water phase were observed to occasionally decrease across the carbon column. This study was undertaken to determine whether bacteria attached to the GAC were primarily the result of growth on GAC or of adsorption onto the GAC.

Experiments to assess initial growth characteristics were conducted in two Teflon columns 20 inches in length and 1.6 inches in diameter (i.d.). These columns were filled with approximately 18 inches of GAC. This is the only mini column experiment in which a bed depth of other than 36 inches was used. The same flow rate (80 ml/min) was used as in the other studies, therefore, the EBCT was approximately 7.5 minutes.

Differential bacterial loadings to the two GAC columns were accomplished by passing the influent water to one of the Teflon columns (see Figure 15) through a 0.22 µm Millipore Filter Cartridge (Millipore Corporation, Bedford, MA). This effectively reduced the density of bacteria in the influent

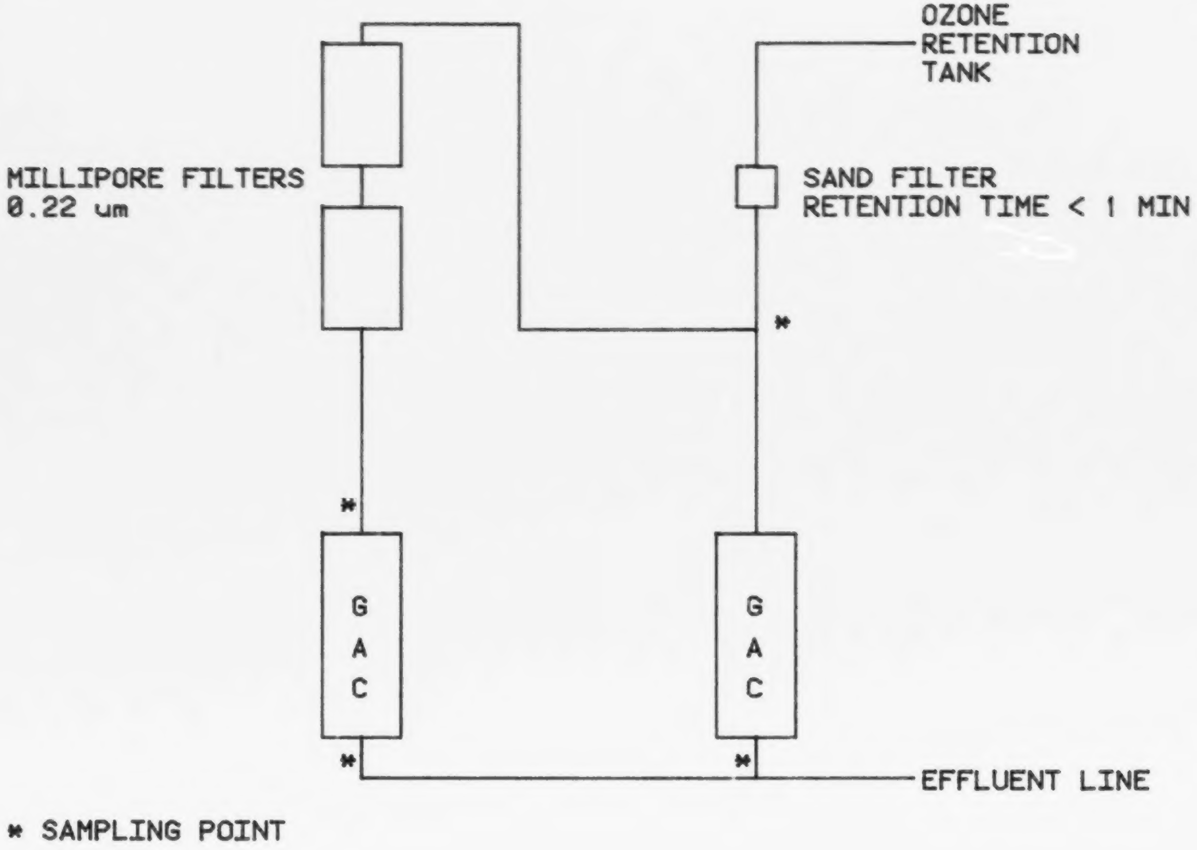

OZONE
RETENTION
TANK
MILLIPORE FILTERS
0.22 um
SAND FILTER
RETENTION TIME < 1 MIN
*
G
A
C
G
A
C
EFFLUENT LINE
* SAMPLING POINT

Figure 15. Bacteria Growth Study Schematic Diagram

water by 50% for the column receiving filtered water. The only parameters monitored on the 20 inch columns were bacterial density in the water phase and on the carbon. This study was conducted starting on day 232 of the long term operation, during mode C, using ambient water.

Carbon for the bacterial loading study was pre-conditioned by adsorption of pilot plant organics for approximately 100 days. Thus, a surface concentration of adsorbed organics was developed to a point well after reaching stable bacterial population on the carbon. The carbon column was then removed from service and placed in an autoclave so that both columns would start in sterile condition.

TOC Removal Rate

The purpose of this experiment was to determine the rate of biological TOC removal on sand as compared to GAC. This determines the applicability of sand as an estimator of bioactivity on GAC. Once the rates of removal on sand and GAC are demonstrated to be comparable, the relative contributions of biodegradation and slow adsorption can be determined. The results can then be used to mathematically model long term TOC removal in a GAC contactor and determine to what extent preozonation may improve GAC performance.

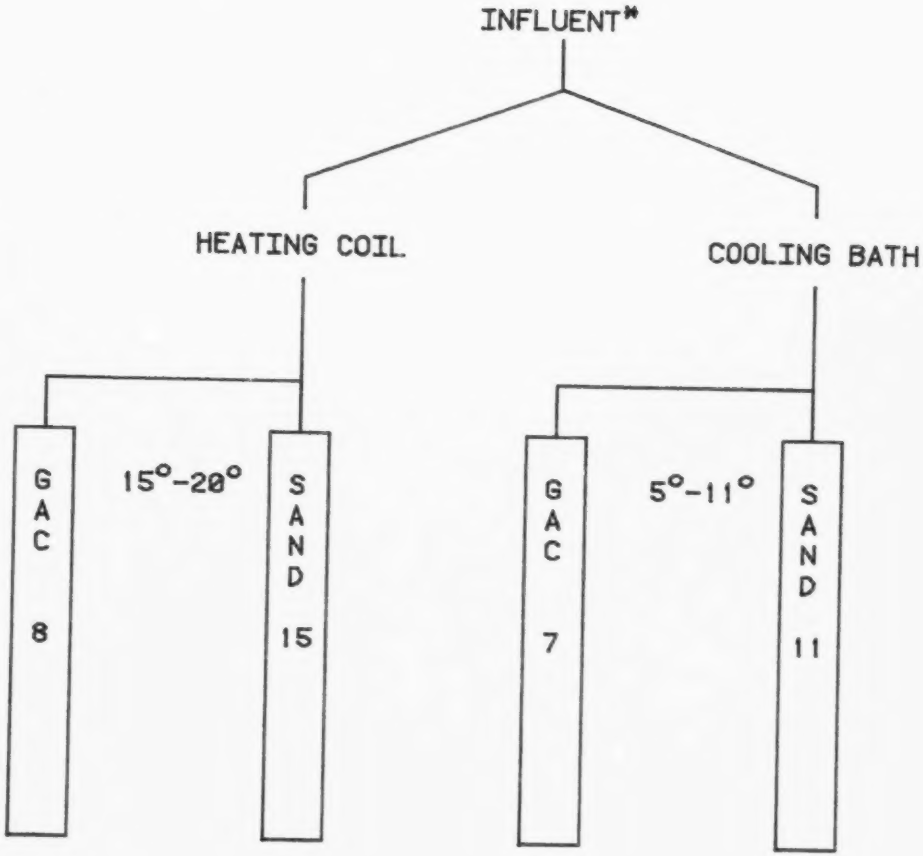
Other investigators (27, 113) have postulated that long term TOC removal observed on GAC is due to a faster rate of TOC biodegradation on GAC than on non-activated media (e.g. sand). Mechanisms proposed for this faster rate include concentration of organics at the GAC surface and acclimization to adsorbed substrate (27). In either case, the concentration of substrate available for biodegradation is increased. Biological TOC removal has been shown to be first order with respect to organic carbon concentration when the organic concentration is below 10 mg/L (124). Therefore an experiment to compare rates of biological removal on GAC and a non-activated medium (sand) was undertaken.

Four contactors, two containing sand and two containing GAC, were operated in parallel at two different temperatures. The GAC contactors were on line >400 days, one sand contactor was on line >200 days and the other sand contactor was on line >140 days. The temperature range on the warm contactor was 15 to 20 degrees centigrade, with the contactor starting at 19, then slowly approaching 15 as the season grew colder before a heating coil was installed, after which the temperature was maintained at 20 degrees. The cold contactor started at 11 degrees and declined to 5 degrees, with the temperature for the last 30 days of the experiment in the range of 5 to 7 degrees centigrade.

One sand and one GAC contactor were receiving chilled influent and the other two contactors were receiving warmed influent. Figure 16 is a schematic diagram of the contactor configuration.

The effect of increased organic carbon available for biodegradation is shown in the following equation. This equation is an expansion of the Arrhenius rate constant equation:

$$|TOC|_R = k_o \exp(-E_a/RT)|TOC|_A$$


INFLUENT*
HEATING COIL
COOLING BATH
GAC 8
15°-20°
SAND 15
GAC 7
5°-11°
SAND 11

* CONVENTIONAL TREATMENT PLUS OZONE

Figure 16. TOC Removal Rate Schematic Diagram

where $[TOC]_R$ = total organic carbon removed biologically, mg/l

$[TOC]_A$ = total organic carbon available for biodegradation, mg/l

It is hypothesized that a greater organic carbon concentration available for bacterial uptake should manifest itself in a greater temperature induced TOC removal differential on GAC than on sand. Figure 17 is an illustration of the hypothesized effects of substrate concentration on TOC removal, assuming first order kinetics. The upper line on the figure shows how TOC removal could vary as a function of TOC concentration for a large rate constant (k at warm temperatures) and the lower line represents a smaller rate constant (k at cold temperatures). In this hypothesis, the upper line would represent the warm contactor and the lower line would represent the cold contactor. The vertical lines represent the TOC removal differential between contactors at different temperatures but at the same substrate concentration. Note that if the bacteria are in contact with a higher concentration of biodegradable TOC on GAC compared to sand, the differential between the warm and cold GAC contactors is hypothesized to be greater than that for sand. The overall result expected is a greater differential mass loading on GAC than on sand if enhanced bacterial removal is occurring on GAC as compared to sand.

Another aspect of this experiment is that a measurement of the overall rate constant on GAC can be determined. If we assume that first order removal prevails for TOC under the experimental conditions (based on Zobell's work, 1943), then the TOC is within the range of first order TOC removal for organic carbon. More recently, Lawrence and McCarty, (136), measured kinetic constants for wastewater effluent and determined that the Ks for chemical oxygen demand (COD) was on the order of 22 mg/l. This is viewed as a conservatively low estimate for the relatively unpolluted water used at Torresdale. Assuming that degradation of readily biodegradable material occurred prior to application to the GAC contactor, the predominant organic material would be recalcitrant.

An estimate of the COD in the influent to the carbon columns was made based on the influent TOC to the GAC contactors and previous operating data for Torresdale (COD for finished water averaged 8.0 mg/l, Gasiewski, (137)). During the period that COD averaged 8.0 mg/l, TOC averaged 2.6 mg/l for finished water and 1.6 mg/l for influent to the bench scale contactors. Using the averages, and the ratio of finished water COD/TOC of 3.08, the COD in the influent is estimated at 4.9 mg/l. This is well below the Ks and indicates that the data will lie on the linear portion of the Michaelis-Menten curve relating uptake velocity to substrate concentration.

Assuming that the TOC removal rate (or uptake velocity) is a linear function of substrate concentration should allow an estimate of the overall rate of biodegradation on GAC by comparing the temperature induced TOC differentials on sand and GAC. Thus, the rate of biodegradation on GAC can be determined as:

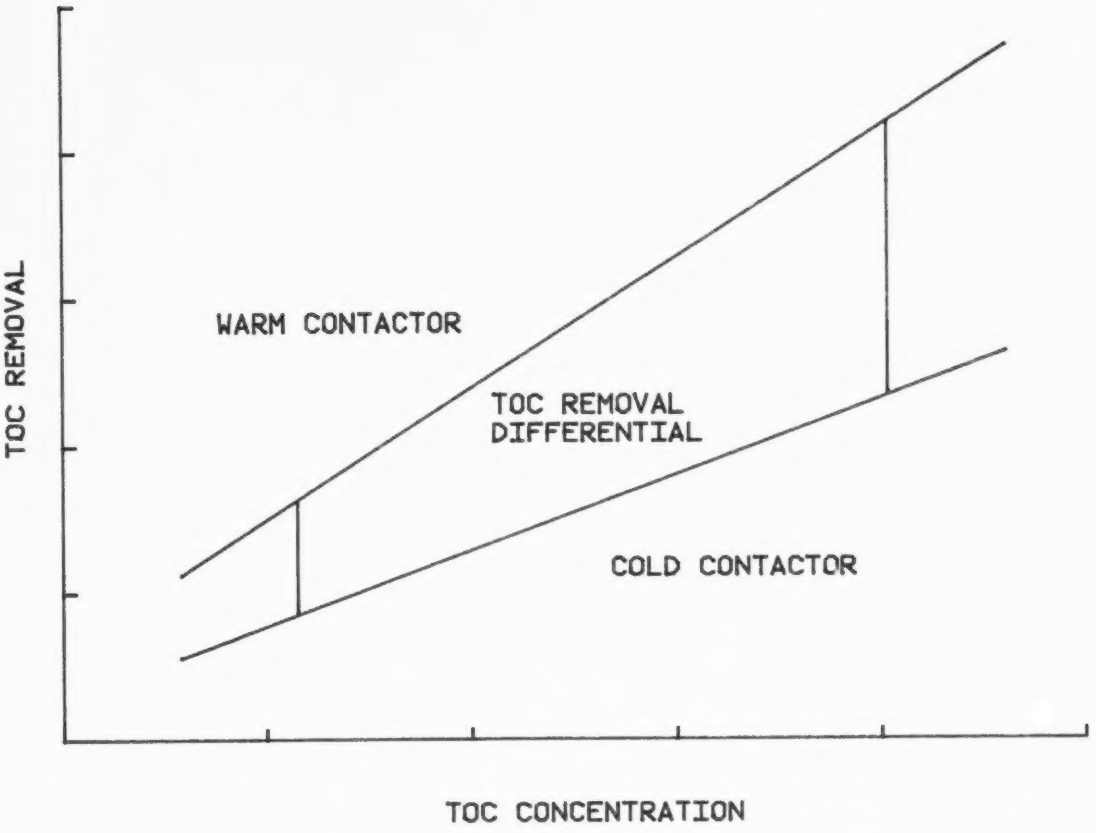


Figure 17. Relationship of TOC removal to substrate concentration.

$$GACr = (GACd/SANDd) \times TOCr$$

where GACr = magnitude of biological removal on GAC
GACd = difference in TOC removal between warm and cold GAC contactors
SANDd = difference in TOC removal between warm and cold sand contactors
TOCr = magnitude of TOC removal on sand

The rate of biological removal could be determined on either the cold or warm GAC contactor. The cold GAC contactor rate would be estimated by using the cold sand contactor TOC removal as TOCr and the warm GAC contactor removal would be based on the warm sand contactor removal as TOCr.

SECTION 6

EXPERIMENTAL

Testing for the pilot-scale studies was divided into four major areas: organic, inorganic, physical and microbiological. Table 14 presents a summary of the specific analyses performed; any new methods are described in detail below. A description of analytical methods used in the bench-scale ozone studies concludes this section.

ORGANIC

Samples were normally collected once per week as a 30 minute composite sequenced to account for the detention times of the unit processes. The effluent from each site was collected in a 4 liter serum bottle at the pilot plant site, through teflon sampling lines and then brought immediately to the laboratory where it was placed in appropriate bottles for storage at 4°C. Samples for volatile organic analysis were stored in 40 mL clear screw-cap vials with teflon-lined septa. Samples were dechlorinated with sodium sulfite. Holding times prior to analysis averaged 7-14 days for chlorinated volatiles and 14-28 days for non-chlorinated volatiles. A 28-day composite of effluents from selected sites in the treatment train was also made from daily grab samples which were stored at 4°C.

Dissolved organic carbon (DOC) and ultraviolet (UV) samples were acidified to pH 2 with phosphoric acid and stored in 160 mL serum bottles with teflon lined septa at 4°C. Prior to analysis these samples were pressure filtered through a 0.2 micron surfactant free polycarbonate membrane to remove carbon fines. All results expressed as total organic carbon (TOC), therefore, are DOC. Holding times prior to analysis were 7-14 days for DOC and 60 days for UV. TOX samples were stored in 160 mL bottles with teflon lined screw caps at 4°C. Holding times prior to analysis were 14-28 days.

Volatiles by Purge and Trap Method

Volatile halogenated organic analysis was performed utilizing a Hall detector according to EPA Method 601 (138) with two minor modifications. A ten foot glass column was used instead of an 8 ft. column and the temperature program was 60°C for four minutes and 6°C per minute to 215°C. A list of all volatile halogenated compounds and their minimum quantifiable limits (MQL) are presented in Table 15. During the first part of the study (from 4/15/80 to 3/17/81) the non-halogenated volatile organics (see Table 16) were also analyzed using EPA Method 601 modified with a 16°C per minute programming rate with a flame ionization detector. During the second part of the study (after 3/17/81) a hydrophilic purge and trap technique was used that was developed by the U.S. Geological Survey Water Resources Laboratory (139). In this technique the sample was "salted out" with sodium sulfate

TABLE 14. CHEMICAL, MICROBIOLOGICAL, AND PHYSICAL TESTS

- A. Organic
  - 1. Volatiles by Purge and Trap Method
    - a. Halogenated (138)
      - i. Trihalomethane Instantaneous (THMI) (138)
      - ii. Trihalomethane Formation Potential (THMFP)
    - b. Non-Halogenated (138,139)
  - 2. Semi-Volatiles (extracted by macroreticular resin)
  - 3. Organic Carbon Analysis
    - a. Dissolved Organic Carbon (140)
    - b. Organic Halogen (141)
      - i. Total (TOX)
      - ii. Purgeable (POX)
      - iii. Non Purgeable (NPOX)
    - c. Ultraviolet (UV) Absorbance at 254 nanometers (A254)

- B. Inorganic
  - 1. Metals (Group 1 & 2) (103)
  - 2. Nutrients
    - a. Nitrate (103)
    - b. Ammonia (142)
    - c. Phosphate - Total (103)
  - 3. pH (103)
  - 4. Dissolved Gases
    - a. Oxygen (143)
    - b. Carbon Dioxide (140)
    - c. Chlorine (103)
  - 5. Ozone
    - a. O_3 - gas (103)
    - b. O_3 - solution (144)

- C. Physical
  - 1. Turbidity (103)
  - 2. Temperature (103)
  - 3. Odor (103)
  - 4. Head Loss
  - 5. Flow

- D. Microbiological
  - 1. Standard Plate Count (103)
  - 2. Coliform (103)
  - 3. Soil Extract Agar (App. C)
  - 4. Actinomycetes (103)
  - 5. Nitrifying Bacteria (145)
  - 6. Endotoxin
  - 7. Fungi (103)
  - 8. Speciation (146,147,148,149)

TABLE 15. HALOGENATED VOLATILE COMPOUNDS (138)

Compound	MQL	GC RRT[a]	GC/MS RRT[b]
Methylene Chloride (MECL)	0.1	0.56	0.61
Chloroform (CHLO)	0.1	1.00	1.00
1,2-Dichloroethane (DCE2)	0.1	1.07	1.06
1,1,1-Trichloroethane (TCE1)	0.1	1.17	1.17
Carbon Tetrachloride (CTET)	0.1	-	-
Dichlorobromomethane (DCBM)	0.1	1.25	1.23
1,2-Dichloropropane (DCP2)	0.1	1.35	1.33
Trichloroethylene (TCE)	0.1	1.41	1.40
Dibromochloromethane (DBCM)	0.1	-	-
Bromoform (BROM)	0.1	-	-
1,1,2,2-Tetrachloroethylene (PER)	0.1	1.81	1.07
Bis(2-chloroethyl) ether (BCEE)	0.3	2.13	-
Chlorobenzene (CBEN)	0.1	2.03	2.07

MQL = Minimum Quantifiable Limit

[a] Relative Retention Time (RRT) of Chloroform is 10.7 Minutes, (Table 16)
See Appendix A, for GC Retention Time Stability Data

[b] Relative Retention Time (RRT) of Chloroform of 15.9 Minutes

TABLE 16. NON-HALOGENATED VOLATILE COMPOUNDS (139)

Compound	MQL	GC RRT[a]	GC/MS RRT[b]
Acetone (ACET)	0.5	0.60	0.66
Dimethoxymethane (DMM)	0.3	0.82	0.86
Benzene (BEN)	0.1	1.44	1.42
Toluene (TOL)	0.1	1.90	1.98
Ethylbenzene (EBEN)	0.1	2.27	2.24
Cumene (CUM)	0.1	2.57	-
Para-xylene (XYL2)	0.1	2.82	-
Ortho-xylene (XYL3)	0.1	2.94	-
1,2-Dichlorobenzene (DCB2)	0.1	3.60	-

MQL = Minimum Quantifiable Limit

[a] Relative Retention Time (RRT) of Chloroform is 10.7 Minutes.
See Appendix A, Table A-12 for GC Retentiom Time Stability Data

[b] Relative Retention Time (RRT) of Chloroform of 15.9 Minutes

TABLE 17. GC OPERATING PARAMETERS FOR NON-HALOGENATED COMPOUND ANALYSIS[a]

Dates	Instrument[b]	Chloroform Retention Time
1) 4/20/80-6/22/80	Tracor Model 222	11.9 min
2) 6/23/80-8/17/80[c]	Hewlett Packard Model 5711	7.7 min
3) 8/18/80-9/8/81	Tracor Model 222	9.5 min
4) 9/9/81-9/14/81	Hewlett Packard Model 5711	9.9 min
5) 9/15/81-12/3/81	Hewlett Packard Model 5711	10.5 min

[a] Packing: 1% SP-1000 on 60/80 mesh Carbopack B, Initial Temp.: 60°C (4 minute hold), Final Temp: 220°C, Temperature Programming Rate: 16°C/min.

[b] Flame Ionization Dectector

[c] Column Length: 10 feet except #2: 8 feet.

and heated to 50°C while the vapor above the liquid was purged for 15 minutes. This hydrophilic technique was used in order to obtain better accuracy and precision for acetone analysis. Using this method the standard deviation for acetone quality assurance samples was reduced from 2.5 ppb to 0.8 ppb and the average recovery increased from 81% to 95% recovery with a standard having a true value of 4.3 ppb. A quality assurance program for volatiles by purge and trap is described in Appendix A.

Volatile organic analyses were performed on a Tracor 222 GC or a Hewlett Packard 5711 GC using a Hewlett Packard 335 2C Data System. GC/MS analysis were performed on a Finnigan 4051 GC/MS with INCOS data system. The purging devices were Tekmar LSC units. Relative retention times are presented in Tables 15 through 17.

The method followed for trihalomethane formation potential (THMFP) was based upon the assumption that the average time for water to reach customers is after 3 days. THMFP conditions were set at a temperature of 25°C, pH buffered to 8.5, and a chlorine dose necessary to obtain a 2.5 ppm free chlorine residual after 30 minutes which insured a residual after 3 days.

Formation Potential Rate Studies --

THMFP seven day rate studies were completed five times from August 1979 to June 1981, Figure 18. Except for test #1, in which settled Delaware River water was used, all tests were performed using untreated river water. The water was adjusted to a pH of 8.5, chlorinated and stored at 25°C for 7

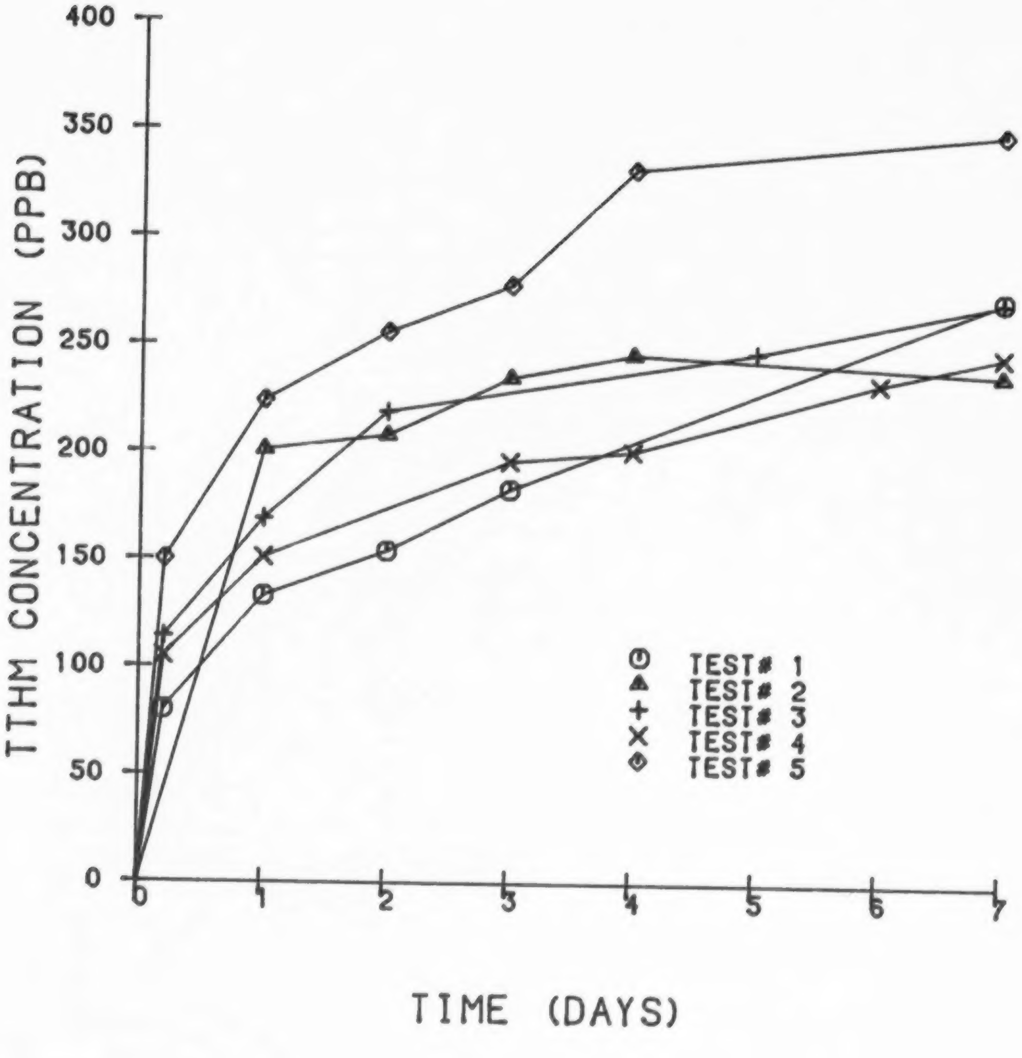


Figure 18. THM Formation Potential rate studies.

days. The rate of formation after seven days was either zero or minimal. In tests #1, 3, 4, 5 there was 29 to 43% formation after 5 hours. There was no 5 hour analysis in test #2. After 24 hours there was 62% formation in tests 3, 4, 5; 49% in test #1 and 85% in test #2. After 4 days 80 to 100% of the seven day formation is complete. Since the number and type of the functional groups on the precursor molecules are not constant, it appears inappropriate to make comparisons between reaction rates.

Semi-Volatiles by XAD Macroreticular Resin Accumulators - Pilot Plant

The XAD resin samplers are glass columns 750 mm long with a 50 mm i.d. The overflow arm was approximately 200 mm from the top of the column. A glass frit at the bottom of the column held the resin bed in place. A Teflon stopcock valve is below the glass frit to be used in the solvent elution portion of the sampling process. The macroreticular resin bed contains approximately 100 ml each of XAD-2 and XAD-8 resin (Rohm and Haas Corp, Phila., Pa.), with an approximate bed depth of 10 cm. Since the XAD-2 has a slightly lower density than the XAD-8 it tends to be on top of the resin adsorbent bed.

A Masterflex peristaltic pump with variable speed control (Cole Palmer Co., Chicago, Ill.) is used to meter the water sampled through the resin adsorbent. The pump is downstream of the resin bed so that no contamination from the pump will reach the resins.

Sampling and Elution Procedures --

The sampling procedure is outlined in Table 18. This procedure was finalized after the first three sampling periods when base neutralization with 0.1 N HCl was changed to 2 x 200 ml wash with distilled water.

TABLE 18. MRR SAMPLER PROCEDURE

A. Mix the sampling reagents in 5 gallons of carbon filtered water to achieve a 10%, by weight, mixture of sodium sulfite and phosphoric acid. A manifold will be set up to deliver the reagents to the sampling columns. Turn on the reagent pump and check the flow rates such that the pH of the sampled water is less than 3.5.

B. Adjust the feed valve to give an inflow rate of approximately 75 ml/min. Open stopcock at bottom of column. Set speed control of the Masterflex pump to 35 ml/min, exactly. Record starting time.

C. Record flow rates through the columns daily and note any problems.

D. After 72 hours, shut off the reagent and sample flows. Then shut off the Masterflex pump and close the column stopcock, making sure the resin stays immersed in liquid.

E. Add 150 ml of ether and drain the column until ether appears in the effluent; then, close the stopcock and wait 10 to 15 minutes. Drain the ether into a clean sample bottle and repeat, using aliquots of 2 x 100 ml of ether. Label the samples.

TABLE 18 (continued)

F. Add 100 ml methanol to the column and wait 10 minutes. Then collect methanol in a sample bottle. Add 200 ml 0.1 N sodium hydroxide and collect the elution. Rinse with 2 x 200 ml of distilled water and wait 10 minutes between elutions. Waste the eluent. (Note: The first 3 samples used 0.1N HCl instead of distilled water.)

G. Add 200 ml methanol to the resin column for storage between sampling periods. Cover every inlet to all components of the samplers with aluminum foil.

Sample Handling and Storage Procedure --

All ether elutions of the resin accumulators were completed on-site and immediately brought back to the laboratory. The ether elutions were transported in 500 ml clear pyrex bottles. Upon arrival in the laboratory, the ether elutions were stored in a freezer at -10°C for a period of 1 to 4 days before concentration by the Kuderna-Danish procedure.

Sample Concentration and Base Extraction Procedure --

The sample concentration procedure prior to gas chromatographic analysis is shown in Table 19. Two additional steps were added to the end of this procedure. First, to remove nonchromatographic acidic materials, a base extraction of the ether sample was performed at pH = 12.0 (0.2N potassium carbonate buffer adjusted to pH = 12 with KOH), at a water:solvent ratio of 10:1. The second step was to add redistilled hexane, (which contains 20 ppm of a C-23 methyl ester internal standard) to the base extracted ether sample. The hexane is added as a "keeper" and the final volume of the sample is adjusted to 1.7 ml. Since hexane has a higher boiling point than ether, the sample will have fewer evaporative losses due to handling and storage. Once the concentration step was completed, the 1.7 mL vial was stored at -10°C until GC analysis was performed.

TABLE 19. DRYING AND EVAPORATION PROCEDURES

A. Prepare a dry ice-isopropanol bath. Temperature should be between -10°C and -20°C.

B. Swirl the sample bottle to remove any water droplets from the ether surface and immerse the bottle in the dry ice bath. Continue gentle movement until all of the water is frozen out.

C. Pour the sample through a 1 inch column of Na_2SO_4 into a 500 ml Kuderna-Danish (KD) flask. To prepare the Na_2SO_4 column, take a short column, plug the bottom with silanized glass wool, and fill with 1 inch of Na_2SO_4. The column should be rinsed slowly with 20 ml of ether before use.

TABLE 19 (continued)

D. Rinse the column into the KD flask with 20 ml of ether.

E. Quickly transfer the ether into a scrupulously clean 500 ml KD flask with a 10 ml receiver.

F. Allow the ice to melt. If there is much ether present, add 25 ml clean ether, refreeze, pour the ether through the column and into the KD flask.

G. Put a clean ebbulator in the KD flask, using tweezers with the bent end up.

H. Put a Snyder column on the KD flask.

I. Put the flask in a warm water bath. The ether should boil smoothly. The upper ring of condensation should be kept on the ground glass joint at the top of the Snyder column. This can be adjusted by (1) raising or lowering the height of the KD flask, (2) raising or lowering the hood door, (3) adjusting the steam valve, (4) adjusting the water level and (5) putting aluminum foil around the KD apparatus.

J. Check the evaporation frequently. When the liqiud level is reduced to approximately 6 ml, the flask should be removed quickly. Make sure the ether condensing in the Snyder column washes the entire inside surface of the KD flask. If the ether level goes below 4 ml note this on the data sheet.

K. Remove the Snyder column, rinse the ebulator and flask into the receiver with 1-2 ml ether.

L. Remove the flask and replace with a micro-Snyder column.

M. Place the receiver in the KD heating block, break off the end of the ebbulator, attach a Nitrogen gas line to the ebulator and adjust the N_2 flow to approximately 1 bubble per second. The heating block should be 28-30°C.

N. Evaporate to approximately 0.75 ml.

O. Remove the N_2 line, rinse the ebulator and receiver with a few drops of ether. Bring the volume to 1.0 ml.

P. Add 5 µl hydrocarbon standards with a clean syringe.

Q. Pour the sample into a clean 2 ml screw top vial. Firmly attach the top and check to make sure that the top in on tight. The Teflon side of the septum should face inside the vial. Do not touch this side of the septum with anything but clean tweezers. Label the vial clearly and put it in the freezer.

The presence of high molecular weight nonchromatographable materials in the ether elution from the MRR samplers created severe capillary column chromatographic analysis problems. These problems included the presence of a large rising and falling baseline, an unstable flame ionization detector (causing an unexpected rise in the level of baseline noise), contamination of the stationary phase of the chromatographic column, and contamination of the injector's internal parts. These problems were especially severe on the samples from the rapid sand filter effluents, ozonator effluents and the sand contactor effluent from the pilot plant.

A solution to the above problems became a major research effort so that reliable analysis could be performed. After several methods of capillary column reconditioning were tried, it was decided that the removal of the nonchromatographic materials from the sample was a better course of action. A review of the literature suggested that the nonchromatographable materials in the samples may be humic acids. Humic acids may be considered di-protic with carboxylic and phenolic groups. The respective pK_a's are approximately 4.8 and 10.5. Thus, base extraction looked like a possible method of removing the analysis interferences. After success in improving chromatography of the sample by base extraction at pH=12, the extraction procedure was modified and optimized. In addition to the extraction of the interferences between the organic and aqueous phases, an acid-base titration was also taking place. Therefore, to achieve consistent removal of interference, the base was buffered to prevent large changes in the base pH (see Figure 19). A 0.2$\underline{N}$ potassium carbonate solution was chosen as the strong buffer. This buffer was selected because of its stability and because it does not absorb in the UV-Visible spectrum. Optimization of the base extraction procedure was completed by UV spectrophotometry at A254. The final extraction procedure is shown in Table 20. This procedure was successful in creating a sample compatible with a capillary GC column and "direct on-column" injection.

Gas Chromatography --

The samples were analyzed on a GC capillary column. The capillary column was a permanently bonded phase equivalent to SE-30. It had a 0.25 μ thick film, fused silica column 60 m long and of 0.32 mm i.d. The injection method used was "direct on-column" with a Carlo Erba 2150AC gas chromatograph equipped with a flame ionization detector. The detector temperature was 275°C. The temperature program was:

62°C - 7 minutes initial isothermal
62°C to 295°C @ 2.5°C/min
295°C - 15 minutes final isothermal

The detector signal is fed to a Columbia Scientific Industries Supergrator 3, which digitally integrates and reports each peak. The integrator data is stored on magnetic tape by transfering the integrated peaks to a Tektronix 4051 minicomputer.

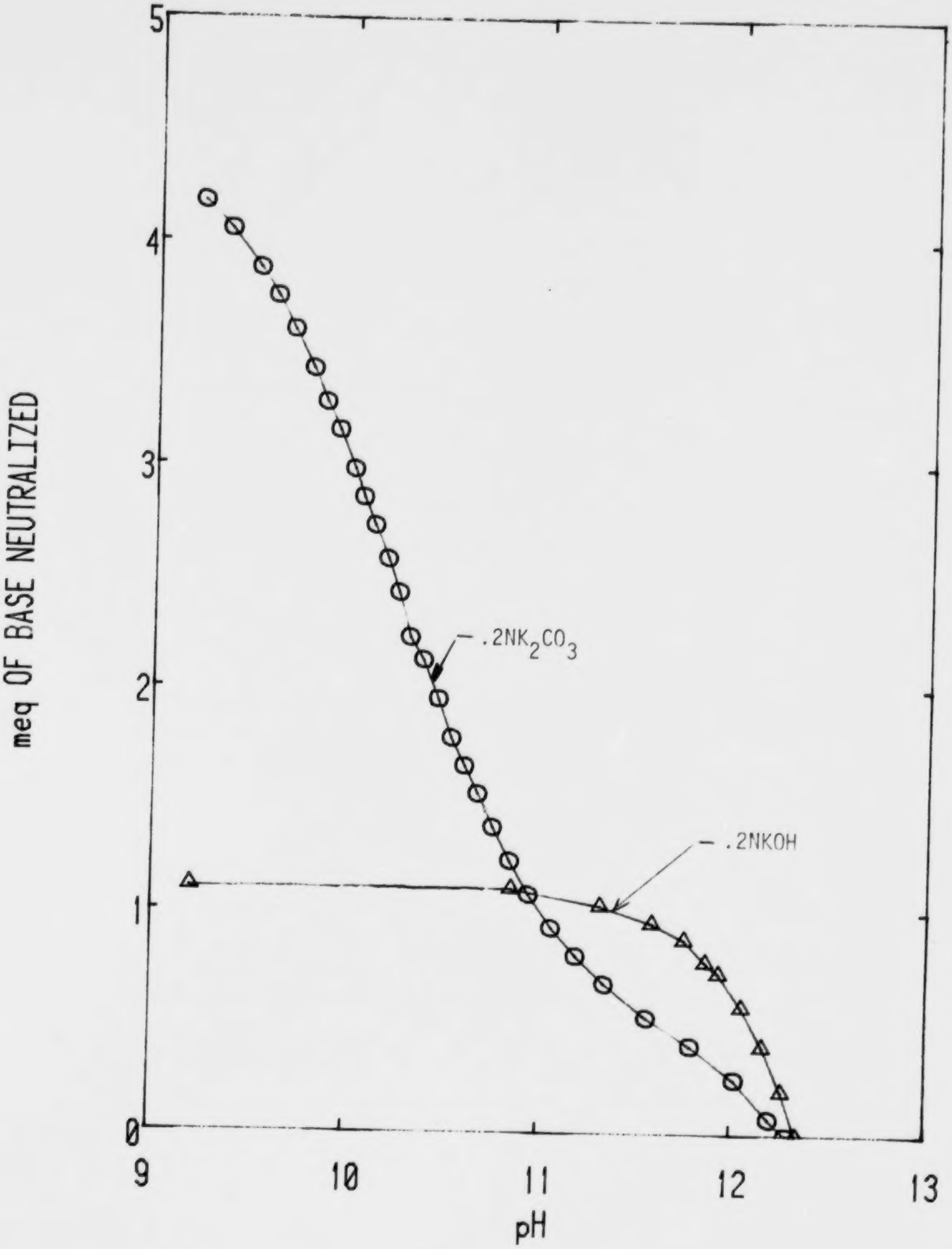


Figure 19. Buffering for MRR samplers.

TABLE 20. BASE EXTRACTION PROCEDURE

A. Make up a 0.2N K_2CO_3 solution and adjust it to pH = 12 with concentrated KOH.

B. Extract the pH 12 solution with redistilled ethyl ether at a 10:1; H_2O: Solvent volume ratio to remove trace impurities.

C. Cover the pH 12 solution with 10 ml ethyl ether for storage

D. Add 10 ml of the base solution to 1 ml of the ether extract in a screw cap test tube. Close the test tube with a Teflon/rubber septum cap.

E. Shake 5 minutes.

F. Centrifuge at 500 g to separate the phases.

G. Freeze out water phase.

H. Transfer ether phase to a storage vial.

I. Add hexane to the storage vial up to 1.7 ml.

J. Check pH of base after extraction[a]

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[a] Note: If the pH is lower than pH = 11, then either increase water:solvent ratio, increase pH of base or change the buffer.

Computer Reconstructed Chromatograms for Pilot and Torresdale Plant --

The chromatographic data stored on magnetic tape is compared to the original chromatogram, edited and converted into the Kovat Index Retention Time Scale. Then the data is plotted in Kovat Index vs. response in a vertical line or spike representation. The number of integrator counts for each peak are normalized to a standard (C-23 normal alkane). The C-23 alkane was chosen because it elutes in a region of the chromatogram containing few peaks. The middle of the response scale would be equivalent to 60 ng/l in the original water sample assuming 100% resin extraction, elution and solvent evaporation.

A typical example of a reconstructed chromatographic profile is shown in Figure 20 for a set of standards. The normalized responses are shown on a logarithmic scale in all the chromatograms in this report. The quality assurance program (Appendix B) shows that data can only be used for semi-quantitative, order of magnitude estimates as small differences between peaks in the same profile or different profiles are not significantly different. The quality assurance program indicates that a significant change in detector response would be a multiplicative factor of approximately 3 for 95% confi-

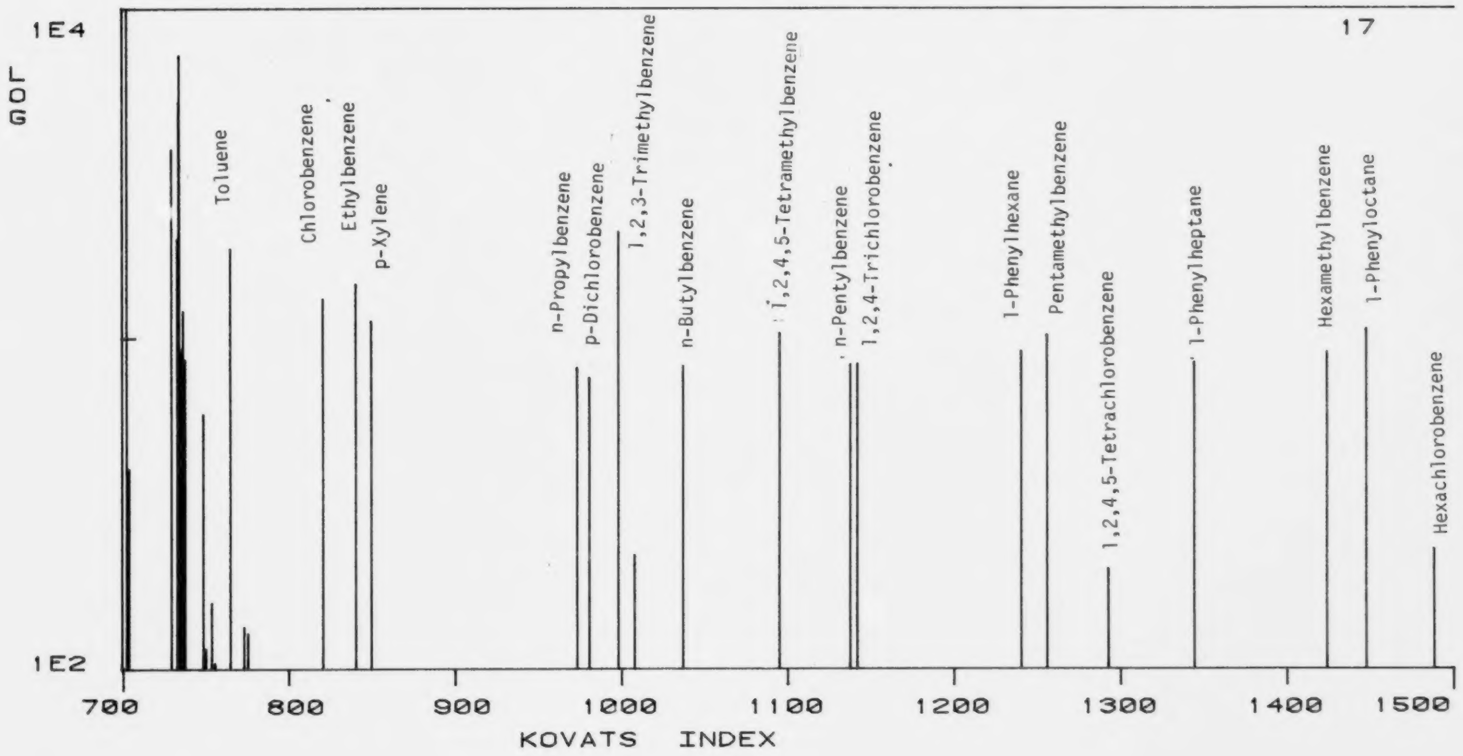


Figure 20. Reconstructed chromatographic profile.

dence. When normalizing the peak responses to a fraction of some standard, the distribution of detector response or spike heights is skewed. However, the logarithm of the ratio removes the distortion so that normal distribution statistics may be used.

Numerical Analysis to Compare Computer Reconstructed Chromatograms --

The application of Chi square contingency tables as a statistical method to compare how different two or more broad spectrum chromatographic profiles was used in this study. Past efforts in interpreting broad spectrum gas chromatography have relied on subjective evaluation of the chromatograms (34,37). There was no scale to determine differences between chromatograms by "how much" unless selected individual peaks were studied.

The Chi square technique offers many potential benefits:

1. A scale to indicate significance level of difference,
2. Determination of regions or categories of greatest differences between chromatograms,
3. Determination of changes in response for a given retention time if classifications are so set,
4. Flexibility in setting up classifications to fit peculiarities of chromatograms,
5. No assumption of distribution to meet, and
6. Weighting factors may be applied to each classification in the contingency table to reflect environmental risk or hazard.

The application of Chi square to chromatographic data is new. Some comparisons using Chi square contingency tables presented in this report are:

1. Comparison of uniformity of influent water to an ozonation process.
2. Comparison of uniformity of influents and effluents from an ozonation process.
3. Comparison of uniformity of GAC influent water to GAC contactors over a period of 14 weeks.
4. Comparison of uniformity of effluents of GAC contactors for 14 weeks.
5. Comparison of breakthrough of XAD-2/8 resins composite accumulators.

Chi square analysis is defined by equation (1)

$$\chi_2 = \frac{\sum(f_i - F_i)^2}{F_i} \qquad (1)$$

where f_i is the observed frequency in class i and F_i is the expected (theoretical) frequency in class i. The Chi square analysis is a non-parametric, enumeration statistical method (150). It is the crudest method of pattern recognition and relies only on frequencies in the specific classes or categories examined. Detailed explanations of χ^2 contingency tables are available elsewhere (150).

The application of contingency table to broad spectrum GC profile chromatograms is based on dividing the chromatogram into regions whose boundaries are in terms of retention time and detector response as shown in Figures 21 and 22. Additionally, in the case where there are 18 internal standards, the separation by an arbitrary retention time is replaced by the retention time of an internal standard. This procedure meets one of the primary requirements of Chi square: the categories to which peaks are assigned and then counted must be mutually exclusive. The second requirement is that each peak be determined independently of each other during the assignment.

The Chi-square test for homogeneity (H_0) was performed on the chromatograms in each contingency table. The null hypothesis in the test for homogeneity was that the proportions of the peaks in each corresponding category in each chromatogram was the same (see Figure 22). In this way, the distribution of peaks in the categories which comprise the region of interest in the chromatograms are compared. Once the general test for homogeneity has been performed and rejected, further insight into the nature of the differences found in the general test can be gained by partitioning or pulling apart the matrix of Kovats Indices and detector response categories into smaller contingency tables. The new contingency tables are then tested for homogeneity again, which isolates the categories causing the null hypothesis to be rejected.

There are many limitations to Chi square contingency table analysis as follows:

1. Chi square is sensitive to zero counts for a category.
2. Chi square will not detect small differences.
3. The statistical power of Chi square does not increase at a practical level past 20 categories. (151)
4. At small number of categories, Chi square should be corrected for continuity.
5. Statistical power drops as the total number of peaks per chromatogram decreases. Chi square is not recommended when the total count is 20 or less. Between a total count of 20 and 40, care should be taken when defining the catogories so that counts of less than 5 are avoided for a 2 x 2 contingency table.

The avoidance of zero count per category is not as strict as it once was (143), however, many categories having zero counts should be avoided by combining categories. If zero counts are unavoidable because of analysis restraints, the zero count in the contingency table should be replaced by an arbitrary small number, i.e. 0.5.

The inability to detect small changes is not a great problem in this application. Based on the quality assurance work for the resin samples,the overall precision, as percent standard deviation, is approximately 30%. Thus, the data lends itself to categorical interpretation since the poor precision of the measurement of peak response indicates very little information would be lost during the conversion from internal to ordinal data. The imprecision of the measurement dictates the use of numerical analysis methods not sensitive to small changes that may be part of the sampling and

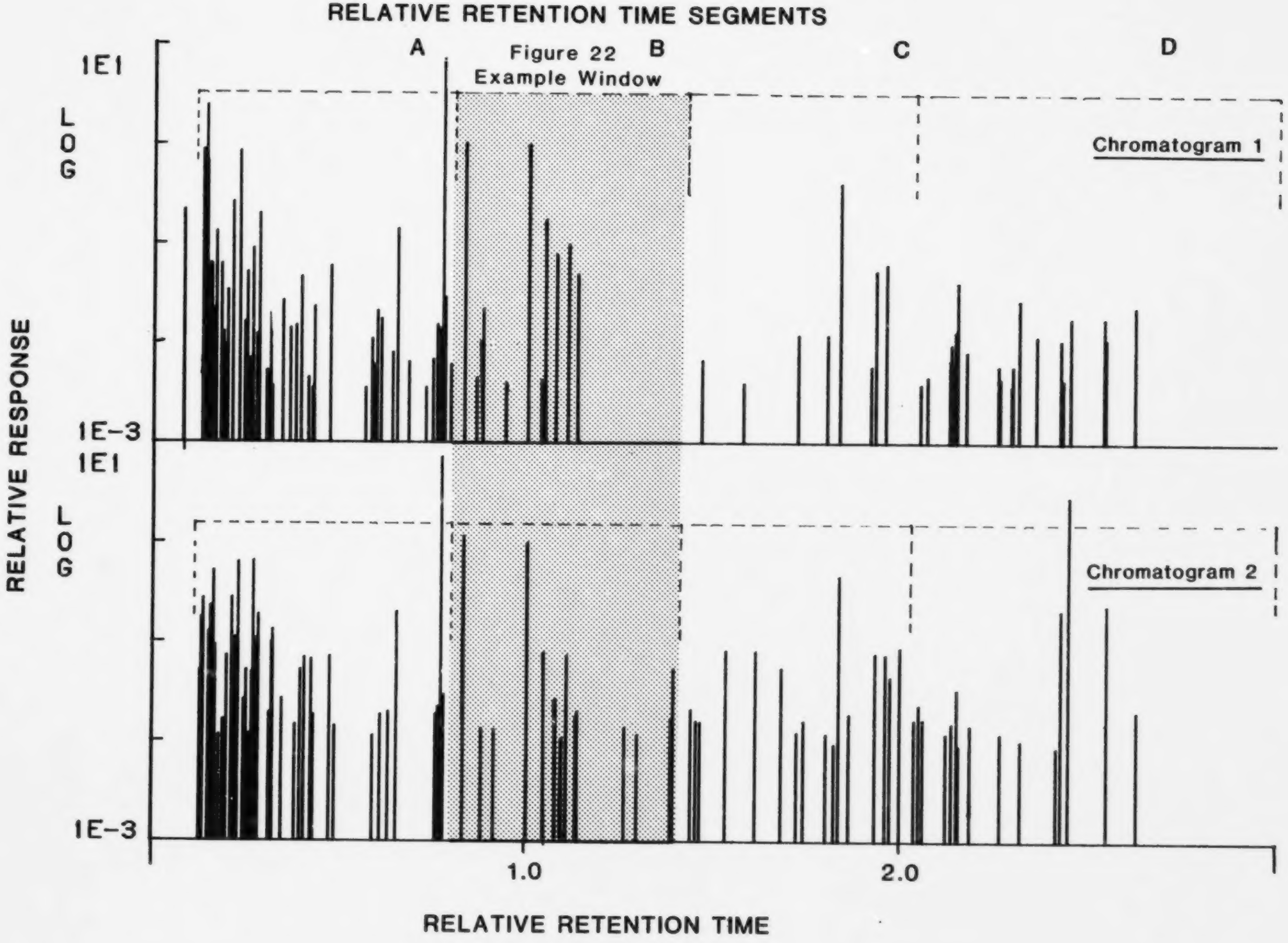


Figure 21. GC profile devisions for x^2 analysis.

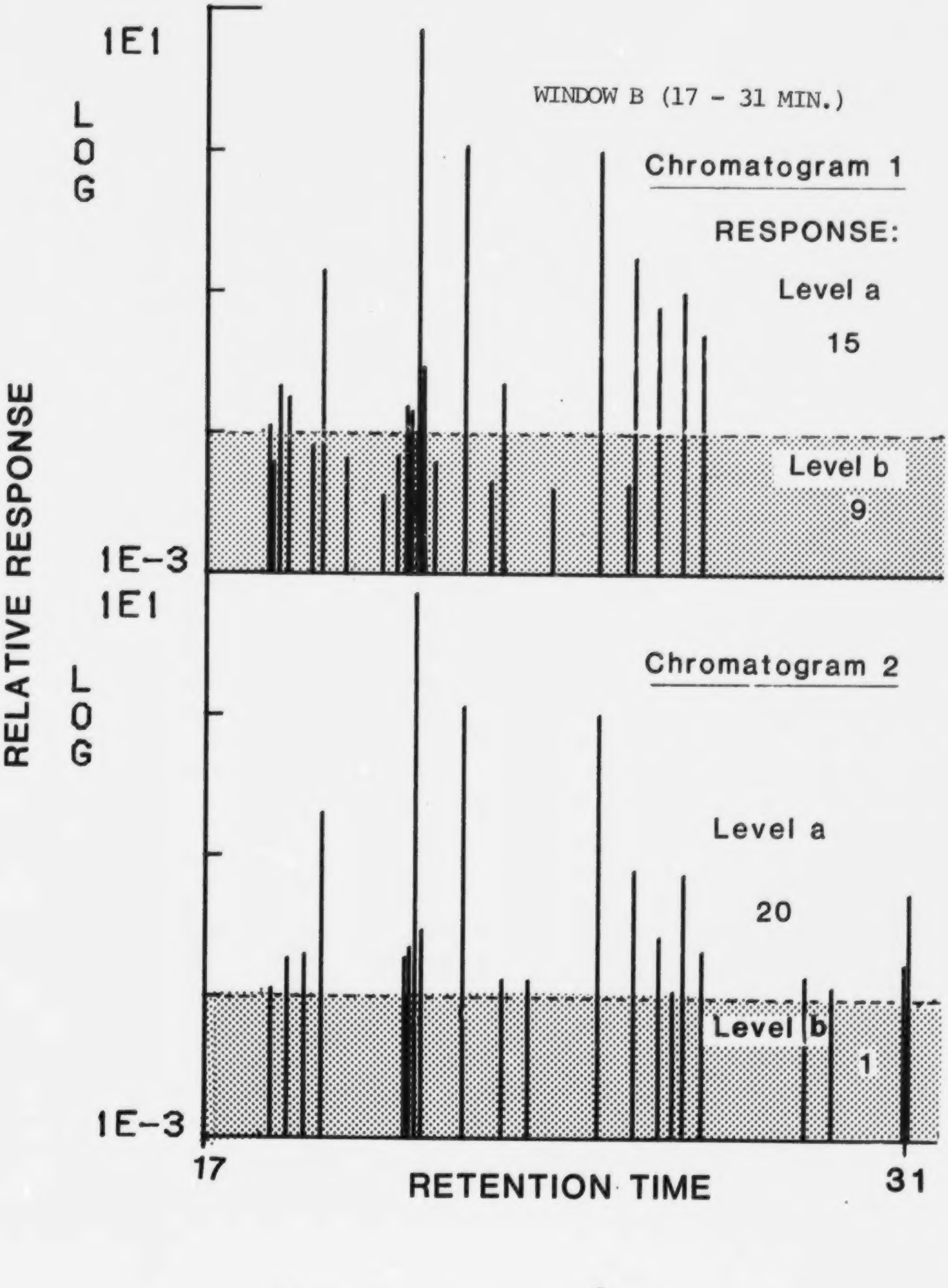


Figure 22. Example of χ^2 analysis.

analytical technique. This is analogous in instrumental terminology to turning down the gain or amplification.

In the application at hand, a bias toward an accepted false null hypothesis of homogenity or no change is preferable to a rejected true null hypothesis. Thus, it is not disturbing even if visual differences are apparent in chromatograms being compared and the chromatograms are shown to be homogeneous at P = 95%.

Semi-volaties by XAD Macroreticular Resin Accumulator - Mini Columns

The MRR sampling for the mini-columns utilized a bed containing 200 ml of (wet) XAD-2 resin. This is different from the pilot plant resin samplers which used a mixed bed of XAD-2 and 8 resins. Each sample represents the extraction of ≈ 340 L of water by an XAD-2 resin accumulator at a pH of 2 and at the temperature of the GAC columns samples. The resin were eluted with 4 x 100 ml of ether. The ether was dried with Na_2SO_4 and concentrated to one ml by two step Kuderna-Danish evaporation as described in Tables 18 and 19. The resultant one ml samples were base extracted using a pH 12, potassium carbonate/potassium hydroxide solution as described in Table 20.

The minicolumn samples were then chromatographed on a 60 meter 0.21 mm i.d. bonded phase SE 30 fused silica, capillary column using a Carlo Erba Model 2050 chromatograph. The samples were analyzed by cold trapping on the GC at:

(1) < 40°C for 2 minutes,
(2) a ballistic rise to 50°C,
(3) 50°C isothermal operation for 3 minutes
(4) 50°C to 260°C @ 3.5°C/min

These chromatographic conditions are different from those used in the Pilot Plant work because of the use of a different GC and injection system and to observe the more volatile compounds. An internal standard containing C-12 and C-18 hydrocarbons was added to each sample. Chromatographic response was plotted on a logarithmic scale (from 10^{-3} to 10) to facilitate a semi-quantitative order of magnitude comparison of the data. This represents an aqueous concentration range of 0.3-3000 ng/l and assumes 100% recovery.

GC/MS analyses were completed on a Finnigin 4051 GC/MS with INCOS data system. GC/MS conditions were indentical to those utilized above.

Organic Carbon Analysis

DOC analysis was performed on a Dohrmann DC-54 Low Level Analyzer using operating procedures as detailed by Dohrmann (140). UV absorbance was determined at 254 nanometers (A254) on a Beckman DB Spectrophotometer using a 40 millimeter cell. Total organic halogen (TOX) analysis was performed according to the method of Dressman, et. al., (141) using a Dohrmann AD-2 Adsorption module and a MCTS-20 Titrating System. Appendix A presents the quality assurance data for organic carbon analyses.

INORGANIC

Samples for inorganic analysis were instantaneous grab samples. Ozone testing was usually conducted three times a week and the samples were analyzed immediately. Dissolved oxygen, carbon dioxide, nutrients and metals tests were conducted biweekly. All samples except the metals were analyzed on the day of collection. Metal samples were preserved with acid and analyzed within EPA recommended time limits. Chlorine testing was conducted weekly. pH testing was performed daily to monitor conventional pilot plant treatment conditions and weekly on ozone and GAC effluents.

Dissolved oxygen was determined by Orion gas sensing electrodes (143). Carbon dioxide was routinely determined using an Orion gas-sensing electrode (144). However for a special study CO_2 was also determined by modifying the Dohrmann DC-54 TOC Analyzer. The lithium hydroxide scrubber was removed from the gas line thereby allowing naturally occuring carbonate and bicarbonate produced during ozonation (from CO_2 at pH 8 to 8.5) to be measured as CO_2 in the DC-54.

Free chlorine concentration was determined according to Standard Methods (103), or by using a Hach DPD Test Kit (153). Total phosphate and total nitrate were determined according to Standard Methods (103) on a Technicon Autoanalyzer II. Ammonia was determined by an Orion gas sensing electrode (142). pH was measured on an Orion 700A Ionalyzer. All metals (see Table 21) were determined according to Standard Methods (103) on Perkin Elmer 503 or 303 atomic absorption spectrophotometer.

TABLE 21. METALS (103)

Group I

(a) Ba - Barium
(b) Cd - Cadmium
(c) Cr - Chromium
(d) Pb - Lead
(e) Hg - Mercury
(f) Se - Selenium
(g) Ag - Silver
(h) Fe - Iron
(i) Ca - Calcium
(j) Mg - Magnesium
(k) Cu - Copper

Group II - Same metals in Group I plus

(a) Na - Sodium
(b) K - Potassium
(c) Mn - Manganese
(d) Zn - Zinc
(e) Al - Aluminum
(f) Co - Cobalt
(g) Ni - Nickel
(i) Ti - Titanium

Ozone

Gaseous ozone analysis was performed using the iodine-thiosulfate Standard Methods Technique (103). Dissolved ozone analysis was performed by a new method using Indigo Carmine based upon the method of Bader and Hoigne (106).

Indigo Carmine Measurement of Aqueous Ozone Residual --
This method presents a significant modification of previous indigo techniques (144) as Indigo Carmine (indigo disulfonate) is used as the color reagent rather than indigo trisulfonate. The latter is unavailable in the United States and must be synthesized. Additionally, this new method avoids stoichiometric calculations and molar quantities. The method is based on the fact that indigo disulfonate (IDS), a deep blue colored conjugated aromatic compound, undergoes stoichiometric oxidation by ozone to produce isatin, an unconjugated, colorless material. The intensity of coloration is proportional to the Lambert-Beer Law at 625 nm, thus, by monitoring the loss of color spectrophotometrically, the amount of ozone present may be deduced.

Materials and Methods -- Indigo disulfonate (IDS), disodium salt certified biological stain from Fisher Scientific.

-- pH 2 phosphate buffer - to about 1800 ml of ozone demand free water is added 50 g of KH_2PO_4 with stirring. When this material has dissolved, the pH is adjusted to 2.0 with concentrated H_3PO_4, and the solution made up to 2 l.

-- About 0.75g IDS (2×10^{-6}M) is dissolved in 1 L ozone demand free water. This is labeled IDS stock solution. 8 ml of stock solution is pipetted into a 1 L volumetric flask and made up to 1 L with phosphate buffer. Due to the relatively low solubility of indigo disulfonate as compared to Bader and Hoigne's indigo trisulfonate (144), the solution should be filtered through a Reeve-Angel AH34 glass fiber filter or equivalent to remove particulates. This is labeled IDS working solution. This solution has a maximum absorbance at 625 nm with a molar adsorptivity of 2.4×10^4 $M^{-1}cm^{-1}$.

-- Spectra were obtained on a Beckman DK-2A scanning spectrophotometer. Quantitative analysis was carried out on the DK-2A and a Bausch and Lomb Spectronic 20. cells used were 1-cm quartz.

-- Concentrated aqueous ozone solutions were prepared by ozonating phosphate buffer with high applied ozone doses.

Calibration -- Since the absorbance of IDS follows Lambert-Beer's Law, the change in absorbance on reaction with ozone should be a direct function of the change in IDS concentration:

A = Absorbance

$\Delta A = \varepsilon \ell \Delta C$ = Molar Absorptivity

ℓ = length

If ℓ is held constant, than ΔA may be used regardless of the absolute concentration of IDS. In lieu of constructing a series of standard curves, use is made of the fact that the reaction between IDS and ozone is stoichiometric and the ratio of the change in IDS concentration (or absorbance) to a given change in ozone concentration should be constant:

$$\frac{\Delta A}{\Delta O_3} = K$$

Since the blank is made from ozone free phosphate buffer rather than ozone, ΔO_3 becomes the ozone residual in the calibration solution and

$$K = \frac{\Delta A}{O_3}$$

In the calibration procedure, concentrated ozone solutions were generated as above. Measured aliquots were withdrawn and split with one being subject to $KI/S_2O_3^=$ titration (103) and the other to indigo.

In a typical calibration run, an ozone applied dose of approximately 90 mg/l was bubbled through phosphate buffer for about 1/2 hour. 50 ml of this solution was transfered to a flask containing 10 ml of 20% KI solution and titrated to the starch endpoint with 0.0100 N $Na_2S_2O_3$. One ml of the ozone solution was pipetted into 25 ml volumetric flask containing about 23 ml working IDS. It was stoppered, shaken, made up the mark with IDS and its absorbance determined at 625 nm. A blank was similarly constructed with 1 ml distilled water in place of the ozone solution.

For a series of 12 measurements, K was determined to be 0.247 ± 0.010 (mean ± 95% confidence interval).

Utilization -- In practice, a measured volume of working IDS is pipetted into two volumetric flasks. One is made up to the mark with distilled water and the other with water containing an ozone residual (test solution). The flasks are then stoppered and shaken and the absorbance is determined at 625 nm. The difference on absorbance is calculated as:

$$\Delta A = (A_{Blank} - A_{O_3})$$

and the residual is:

$$(O_3)_{resid} = \frac{(\Delta A)(V_{tot})}{K\,(V_{O_3})} \text{ (mg/l)}$$

where V_{tot} is the volume of the volumetric flask used (ozone + IDS) and V_{O_3} is the volume of the sample.

For residuals of 0-1 mg/l, 25 ml volumetric flasks and IDS volumes of 5, 10 and 15 ml were found to be sufficient for the lowest to highest concentrations. It should be remembered that ozone is relatively unstable at conditions of water treatment, thus, to obtain an accurate measurement, it must be conducted rapidly, and preferably directly from the ozone contactor. Once the ozone has reacted with IDS, the resultant solution color is very stable. Although some fading occurs in IDS solutions, it appears to be experienced by both the blank and the sample to the same extent and does not present any problem.

Measurements have been conducted to ascertain the effects of other oxidants on IDS. Hydrogen peroxide and Fenton's reagents do not appear to interfere at any concentration. Chloramines and free chlorine at low concentrations (<5 mg/l) also appear to have no effect if the spectral measurement is taken immediately. Some combination of matrix ingredients in the Torresdale Plant effluent produced bleaching not noted in the Pilot Plant. Bleaching of IDS by free chlorine at high concentrations and organic oxidants may occur. This may be prevented by using small amounts of glycine in a differential mode (152), or malonic acid in small quantities, or adding pyrogallol immediately after the indigo reaction with ozone.

PHYSICAL

Turbidity and temperature testing was conducted on a weekly basis. Odor testing was conducted biweekly. Turbidity was measured on a Hach 18900 ratio turbidimeter. Threshold odor was determined according to Standard Methods (103).

In order to insure proper flow conditions throughout the advanced water treatment systems, flow rates through the sand and carbon columns and the ozone contactors were monitored daily. Adjustments, if necessary, were made manually. The flow rates for all systems were initially determined based on empty volume.

Headloss was also monitored daily with the aid of U-tube manometers. Backwashing was initiated when the differential pressure through any column exceeded 10 feet of water. Typically, only the first column in each series required backwashing.

MICROBIOLOGICAL TESTING

Sampling Procedure

Instantaneous grab samples of water were collected in sterile 500 ml Nalgene bottles. Column influent and effluent samples were taken from regulating valves after the water had been wasted for three minutes. Water samples were collected once a week for the Total Coliform and Standard Plate Count Tests and three times a week for the New Soil Extract Agar Plate Count

Technique described below. In addition, samples were collected biweekly for endotoxin, fungi and actinomycetes analyses and monthly for nitrifying bacteria analysis. All samples were taken immediately to the Microbiology Laboratory on the premises and analyzed within three hours.

Granular activated carbon samples were collected three times a week for the first two months and twice a week for the rest of the study. Two ozonated multi-tap columns, one on the Torresdale side and one on the Pilot Plant side, were specifically set up for microbial studies on carbon. Column influent waters were temporarily stopped while approximately 0.5 g (wet weight) of carbon was extracted with sterile forceps and spatula from a tap located midway through the carbon bed. Samples were placed in sealed sterile petri dishes to avoid evaporation.

Carbon samples were also collected when the pilot studies (12-inch GAC columns) were dismantled. One gram carbon samples were collected with a sterile stainless steel spatula at the top of the carbon column and at 2 and 4 feet below the top and handled in the same manner as the multi-tap carbon samples.

The bacteria were eluted from the GAC particles using an ultrasonic procedure. This procedure was based on the ability of ultra sonic vibrations to detach bacteria from submerged surfaces in a buffered solution. Selected carbon samples were divided into 3 subsamples, weighed while wet, and placed in sterile test tubes containing 10 ml of sterile buffered water. These tubes were then placed in an ultra sonic bath for 30 minutes after which the supernatent from each tube was analyzed for bacteria using the Soil Extract Agar Plate Count technique. Subsample results were averaged and recorded as bacteria/gram wet GAC. A more detailed account of this procedure may be found in Appendix C.

Enumeration Procedures

Total Coliforms-Membrane Filtration Procedure--

The total coliform membrane filtration technique (103) which utilizes M-Endo medium, a $35^{o} \pm 0.5^{o}C$ incubation temperature, and a 22-24 hour incubation period, was used to enumerate total coliform densities in water samples. Results were recorded as total coliforms/100 ml and were verified using the API 20E Identification System.

Standard Plate Count Procedure --

The standard plate count (103) was used to enumerate the aerobic and facultative anaerobic heterotrophic bacterial levels in water samples. The term aerobic and facultative anaerobic heterotrophic (AFAH) bacteria has been substituted for total bacteria in this study. The term AFAH bacteria more accurately describes the types of bacteria recovered from both the SPC and Soil Extract Agar (SEA) Plate Count Procedures.

Soil Extract Agar Plate Count Procedure --

A study was made to find a plate count technique capable of recovering a greater number of the AFAH bacteria associated with raw and partially treated waters. Several medias (Soil Extract Agar, R-2A Agar, HV Low Nutrient Agar and Standard Plate Count Agar), temperatures (22°, 28° and 35°C), and incubation periods 2,5,7,10, and 14 days were examined using a standard pour plate procedure. A pour plate technique utilizing Soil Extract Agar, a 28°C incubation temperature, and a 7 day incubation period proved to have the greatest recovery and was used in this study. This technique recovered approximately thirty times more bacteria from carbon column effluents than the Standard Plate Count technique. The detail of this study are described below.

The study was divided into two phases. Each phase was conducted during a one month period when water temperature variations were small. The first phase compared bacterial recovery using 4 different medias, three different temperatures and a seven day incubation period commonly used by European GAC researchers (118). One hundred water samples from 2 GAC column effluents and the Delaware river were subjected to a standard pour plate procedure using 4 different growth medias, SEA, R-2A, SPC and HV agars (Media Composition Appendix C), 3 incubation temperatures (22°, 28° and 35°C) and a seven day incubation period. Two dilutions were made for each sample and each dilution was plated on four different medias and incubated at three different temperatures. Each dilution was done in triplicate. Inoculated plates were immediately placed in plastic bags to prevent plate dehydration and incubated for seven days. Plates were read at the end of this period using a Quebec Colony Counter. Plate count results were numerically similar for the two GAC effluents and the river.

The second phase of this study was conducted after an analysis of data from phase one was completed. This phase compared bacterial recovery at 5 different incubation periods using the media and temperature recommended by phase one. One hundred water samples from the same two GAC columns and the river were subjected to a standard pour plate procedure using SEA agar as the growth media and 22° and 28°C as the incubation temperatures. Two dilutions were made for each sample and each dilution was made in triplicate. Plates were placed in plastic bags and incubated for a total of 14 days. Plates were read at 2, 5, 7, 10 and 14 days of incubation using the Quebec Colony Counter. Plates were kept out of the incubation no more than 2 hours at each reading.

The results of the culture media and incubation temperature study can be found in Table 22 which indicates that bacterial recovery was greatest at 28° (using SEA as the culture media). An analysis of variance (ANOVA) was also done on the data and the results. The results of the 35° and SPC Agar tests were not included in this ANOVA because it was obvious that bacterial recovery rates using either parameter were much lower than those of the other parameters presented in Table 21. The ANOVA showed that there were significant differences in the bacterial recovery of SEA and R-2A culture medias at 22° and 28°C, SEA and HV culture medias at 22° and 28°C, R-2A and HV at 22° but not at 28°C.

The results from the second phase of the study can be seen in Table 23. The greatest bacterial recovery was recorded at 10 days of incubation. At 14 days colonies had spread out and merged and actual colony counts decreased

TABLE 22. PLATE COUNT METHODS DEVELOPMENT: INCUBATION TEMPERATURE AND MEDIA EFFECTS ON PLATE COUNT RESULTS

Media

Incubation Temperature 35°C

	SPC	HV	R-2A	SEA
Samples Analyzed	100	100	100	100
Average Count/mL	120	1700	6600	2810
Standard Deviation	37	610	1480	600
Minimum Count	1	2	16	10
Maximum Count	2900	56700	124800	45500

Incubation Temperature 28°C

	SPC	HV	R-2A	SEA
No. of Observations	98	90	98	98
Average Count	930	17000	22600	84000
Standard Deviation	260	1320	1360	4550
Minimum Count	1	0	530	12400
Maximum Count	7700	55300	60400	284000

Incubation Temperature 22°C

	SPC	HV	R-2A	SEA
Samples Analyzed	100	100	99	95
Average Count/mL	630	4400	18000	59000
Standard Deviation	120	740	100	100
Minimum Count	1	3	100	100
Maximum Count	6900	37400	89600	299000

ANALYSIS OF VARIANCE TABLE

Source	Sum of Squares	Degrees of Freedom	Mean Squares	F	Book F
Temperature (22° and 28°C)	0.2434400 E+10	1	0.2434400 E+10	3.078	5.1
Agar (SEA, R-2A, HV)	0.4195278 E+12	2	0.2097639 E+12	265.237	3.75
Interaction	0.2348155 E+10	2	0.1174077 E+10	1.485	
Error	0.4033358 E+12	510	0.7908545 E+09		

due to confluency of adjacent colonies. Although the recovery was slightly greater at 10 days, the 7 day incubation period was used in this study because it coincided with our work week and also because it was used by Schweisfurth and Werner in European GAC research (122).

A plate count procedure utilizing SEA as a culture media, 28°C incubation temperature and a 7 day incubation period was used for all GAC enumeration studies which involved AFAH bacteria. This modification of the Standard Plate Count Procedure greatly increased the recovery rate of AFAH bacteria from GAC systems.

Actinomycetes-Double Layer Plate Count Procedure --
A double layer plate count technique (103) was used to determine actinomycetes levels in water samples. This technique utilized starch-casein agar plus Actidione, an antifungal antibiotic, as tthe medium, a 28°C incubation temperature and a 14 day incubation period. Results were recorded as actinomycetes/100 mL.

Fungi-Rose Bengal Spread Plate Procedure (103) --
A spread plate procedure utilizing Cook's Rose Bengal agar (pH 4.5) was employed to enumerate fungi in water samples. The inoculated petri dishes were incubated for 7 days at room temperature and the results were recorded as colonies/mL.

Nitrifying Bacteria-MPN Procedure --
Column effluents were analyzed for Nitrosomonas and Nitrobacter using a modified MPN technique developed by Espey, Huston & Assoc., (Document No. 7739). The technique is based on the detection of nitrification, which is indicative of the presence or absence of nitrifying bacteria. Ten tubes of nitrate based medium and ten tubes of ammonia based medium (Appendix C) were inoculated into 10 serial dilutions of each sample. One hundred tubes of each media were therefore required for each field sample. A series of control tubes were also prepared for the detection of inadvertent contamination. One set of controls contained the media with no inoculant, while the other contained the media plus one milliliter of sterile dilution water.

After inoculation, culture tubes were placed in an environmental chamber and incubated at 28°C for 35 days. Nitrification was detected through a nitrite colorimetric test employing Strickland & Parsons (145) nitrite reagent. Nitobacter and Nitrosomonas levels were estimated using the most probable number technique.

Bacterial Endotoxin Analysis Procedure --
Endotoxin levels in the water were determined using a Limulus Amebocyte Lysate Spectrophotometric Method (184) developed and sold by Associates of Cape Cod Inc. under the name Pyrotell. This method uses limulus amebocyte lysate (pyrotell) which forms a clot when incubated with endotoxins at 37°C for one hour. The degree of sample turbidity is then determined using a Baush & Lomb Spectronic 710 spectrophotometer. Endotoxin levels are determined by comparing sample spectrophotometric results with a standard endotoxin curve. Results are recorded in nanograms/mL.

Biochemical Identification Procedures

Total Coliform Identification --

Sheen colonies isolated from the total coliform membrane filtration test were streaked onto SPC agar and subsequently identified using the API 20E system.

AFAH Biochemical Identification Procedure --

Preliminary Pilot Plant studies indicated that the predominant bacteria in the carbon columns and their effluents were gram negative, nonfermenting rods, gram positive spore-forming rods and gram positive cocci. The API 20E Identification System was not able to adequately identify these bacteria. Therefore a more detailed identification procedure was worked out with the help of EPA microbiologists Dan Spino and Don Reasoner. Bergey (146), Weaver (147), Gordon (148), and Gilardi (149) were also used extensively as references. The flow chart in Figure 23 demonstrates the succession of steps taken in the identification process. Only dominant bacteria from the soil extract agar plate count procedure were chosen for identification. Initially, isolation of the dominant organisms in the river and each column effluent were made every two weeks. However, once a mature bacterial community was established on the carbon, changes in species composition occurred more slowly, therefore, isolation of new organisms at this point was done only when new colony types appeared on the SEA pour plates.

TABLE 23. EFFECT OF INCUBATION ON BACTERIAL RECOVERIES

Incubation Temperature 28°C, SEA Agar

Days of Incubation	2	5	7	10	14
# of Observations	25	25	25	25	23
Average Count/ml	13400	25600	33900	50200	39800

Incubation Temperature 22°C, SEA Agar

Days of Incubation	2	5	7	10	14
# of Observations	-0	25	24	14	20
Average Count/ml	300	18200	30200	58000	40900

Scanning Electron Microscopy-Sample Preparation --

Carbon particles were randomly selected from a GAC column with an Empty Bed Contact Time of 60 minutes. This column was part of a previous GAC study conducted by the Philadelphia Water Department at the Torresdale Filtration Plant. Influent water to this column was the same as the chlorinated waters

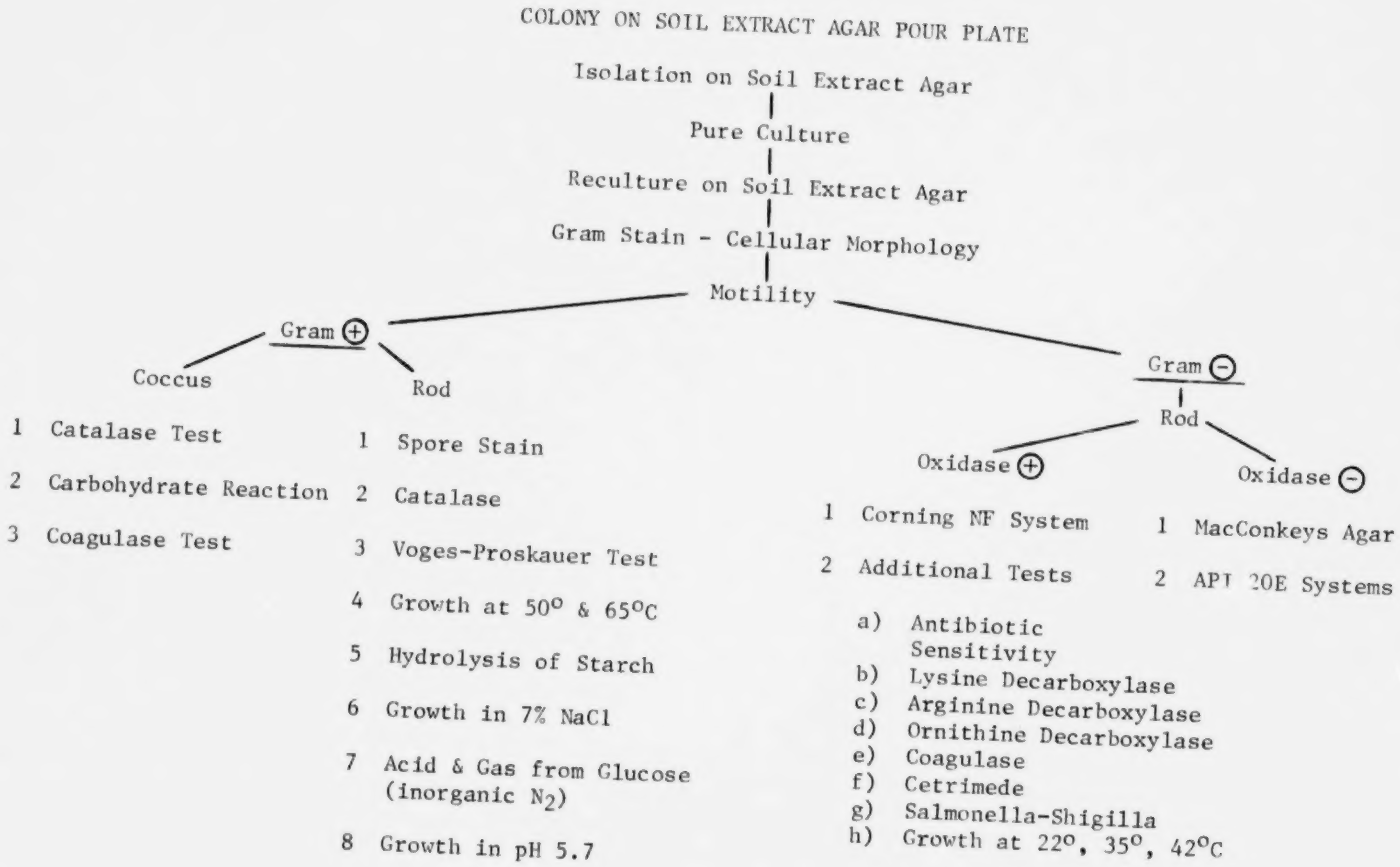

COLONY ON SOIL EXTRACT AGAR POUR PLATE
Isolation on Soil Extract Agar
Pure Culture
Reculture on Soil Extract Agar
Gram Stain - Cellular Morphology
Motility
Gram ⊕
Coccus
Rod
1 Catalase Test
2 Carbohydrate Reaction
3 Coagulase Test
1 Spore Stain
2 Catalase
3 Voges-Proskauer Test
4 Growth at 50° & 65°C
5 Hydrolysis of Starch
6 Growth in 7% NaCl
7 Acid & Gas from Glucose (inorganic N2)
8 Growth in pH 5.7
Gram ⊖
Rod
Oxidase ⊕
Oxidase ⊖
1 Corning NF System
2 Additional Tests
a) Antibiotic Sensitivity
b) Lysine Decarboxylase
c) Arginine Decarboxylase
d) Ornithine Decarboxylase
e) Coagulase
f) Cetrimede
g) Salmonella-Shigilla
h) Growth at 22°, 35°, 42°C
1 MacConkeys Agar
2 API 20E Systems

Figure 23. Total bacteria identification flow chart.

used for the Torresdale Plant GAC columns in the present study.

Sample preparation up to the critical point drying process was done according to Weber et al. (117). The specimens were critical point dryed in a Dep-1 instrument. The dried particles were then mounted on aluminum stubs and spattercoated with 200 A gold. A JEOL-JSM-00A scanning electron microscope was used for observation of the prepared specimen at 25 KV. A picture of the whole particle was taken at low magnification (100x) and then divided into twenty-two 1.5 cm x 1 cm mesh squares. Visual observations of the bacterial densities, locations and types were recorded.

OZONATION: LABORATORY STUDIES

The laboratory conditions under which these studies took place involved many common elements which will be described here. In general samples were analyzed or spiked with the compound of interest, ozonated in a semi-batch diffused gas contactor and then analyzed for the effect of ozone.

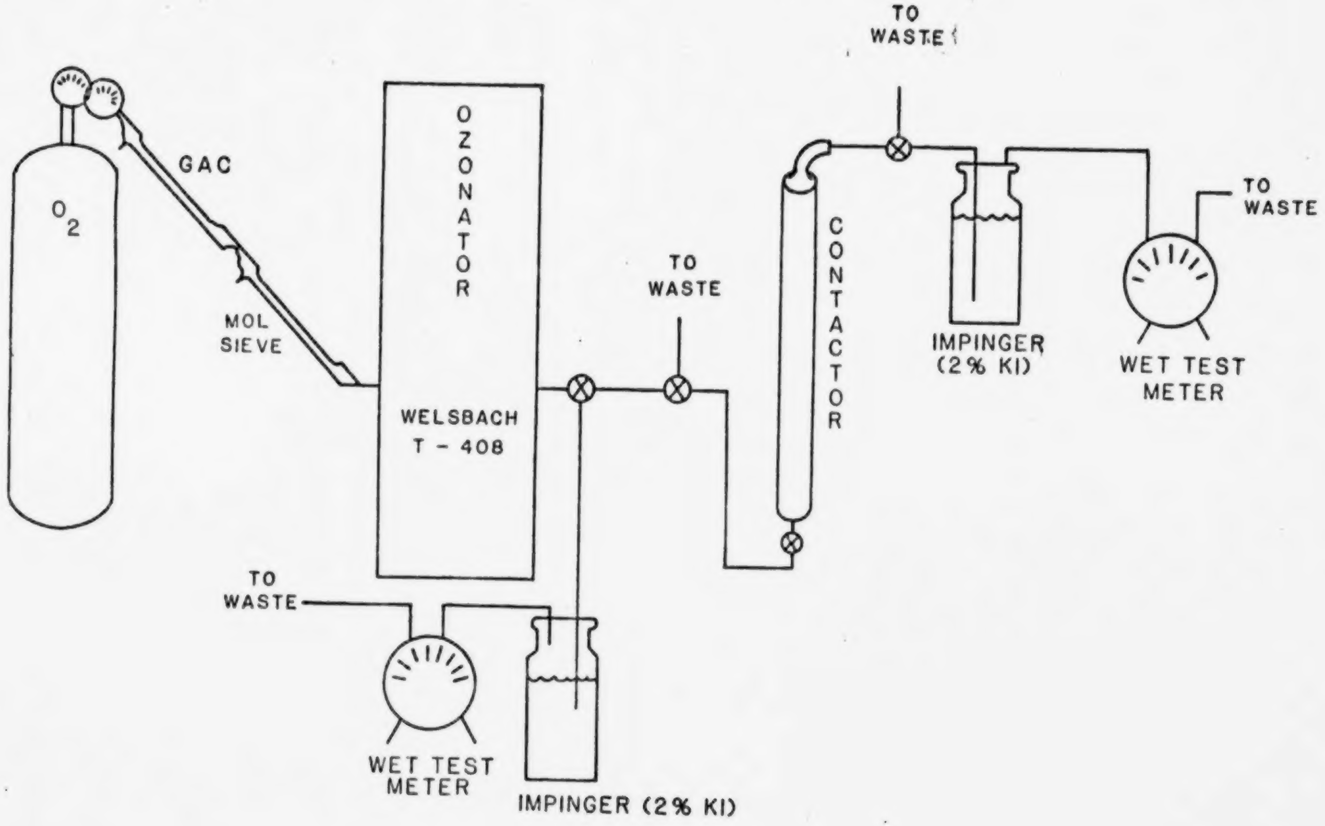
A schematic diagram of the ozonation system may be seen in Figure 24. The feed gas is ultra dry oxygen which is further cleaned by means of a molecular sieve, activated carbon, and a dessicant. Following this, the gas is passed through a flow meter for precisely controlling flow rate after which it is directed into the Welsbach Model T-408 ozone generator where a portion is converted to ozone by corona discharge. The ozone may then travel through one of two paths: into an impinger for analysis or into the contactor for reaction.

Three contactors were used in these studies, however, they were all related with respect to materials and general construction. An example is shown in Figure 25. These contactors were designed such that samples and ozone utilized measurements could be easily taken without greatly disturbing the system. Ozone was analyzed in the gas phase by a variation of the standard methods KI technique and in the liquid phase by reaction with indigodisulfonate.

In a typical reaction kinetics experiment, the ozonator is first equilibrated with regard to dose and the gas phase ozone analyzed. Following this, a measured volume of substrate solution is placed in the ozone contactor. Ozonation is commenced by diverting the gas stream through the contactor concurrently with the starting of a timer. Samples are taken at appropriate intervals based on the anticipated velocity of the reaction. Ozone uptake and mass transfer experiments were accomplished by measuring the concentration of ozone in solution as a function of time rather than the substrate concentration. If there was no substrate in solution, this data was utilized to determine mass transfer rates. In the presence of substrate, this data was utilized to determine the rate limiting (e.g. mass transfer or reaction rate) step in the process.

Methods and Materials

1. Measurement of aqueous ozone was by the indigo disulfonate method (see above).



TO WASTE
O_2
GAC
MOL SIEVE
OZONATOR
WELSBACH T - 408
TO WASTE
CONTACTOR
IMPINGER (2% KI)
TO WASTE
WET TEST METER
TO WASTE
WET TEST METER
IMPINGER (2% KI)

Figure 24. Laboratory scale ozonation system.

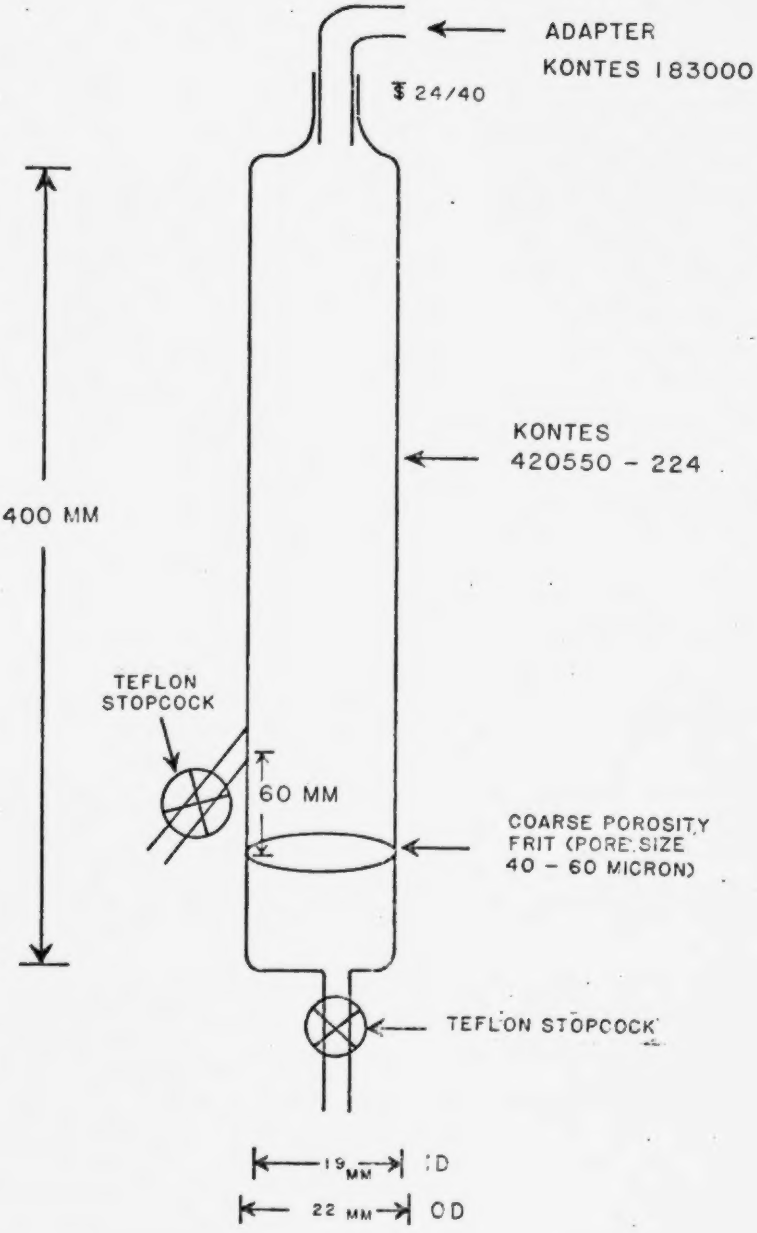

ADAPTER
KONTES 183000
$ 24/40
400 MM
KONTES
420550 - 224
TEFLON
STOPCOCK
60 MM
COARSE POROSITY
FRIT (PORE SIZE
40 - 60 MICRON)
TEFLON STOPCOCK
19 MM ID
22 MM OD

Figure 25. Laboratory scale ozone contactor.

2. Ozonation of organics in water was followed by non-specific parameters, group parameters, and chromatographic analysis. Dissolved organic carbon (DOC) was measured on a Beckman 915B TOC. Optical absorbance was performed on a Perkin-Elmer 559 UV/Visible spectrophotometer or a Bausch & Lomb Spectronic 20. Phenolics were measured with Folin's Test (155), carbonyl compounds by forming the colored adduct after derivatization with 2,4-dinitrophenylhydrazine (154) and glyoxylic acid by a colorimetric technique (163). Diethyl phthalate was measured on a Tracor 550 GC by isothermal direct aqueous injection at 200°C on a six foot glass column of 10% SE-30 on 80/100 mesh Supelcoport. An FID detector was used at 275°C. Data was analyzed on a Spectrophysics SP 1000, computing integrator.

3. Water samples were used as received from the Delaware River or Torresdale Water Treatment Plant. Water reagent preparation or for experimentation was Milli-Q Reagent Grade laboratory water. Ozone demand free water was prepared by exhaustively ozonating reagent water and boiling to dispel residual ozone. For TOC, UV, THMFP, Baker "Water for Trace Organics Determination" was used. In some experiments with micropollutants, water with an inorganic composition that similates the natural composition of the Delaware River was used (Table 24).

4. Glassware was cleaned by washing with detergent, rinsing three times with hot tap water, three times with distilled water and oven drying at 120°C. For special cases, use was made of dichromate cleaning solution, KOH-isopropyl alcohol, 50% HCl, or pesticide quality acetone or hexane. Glassware to be used in the presence of ozone or iodine was conditioned by soaking overnight in solutions of these materials.

5. Sources and purity of organics:

Compound	Source	Purity
Humic acid	Tridom/Fluka or Aldrich	Practical/techinical
Lignosulfonic acid	Baker	Not available
Coniferyl alcohol	Aldrich	99%
Ellagic acid	Tridom/Fluka	Practical
Malvin Chloride	Tridom/Fluka	99%
Coumarin	Tridom/Fluka	greater than 98%
Tannin	Fulka or Fisher	
Catechol	Eastman	98%
Resorcinol	Aldrich	98%
Catechin	Tridom/Fulka	97%
Gallic Acid	Aldrich	Not available
Diethy phthalate	Chem Services	99%
Toluene	Fisher	99%

Other methods are as noted in other sections of this report. Development and application of ozone utilized and spectroscopy as a method of following ozonation are described in the ozonation results section.

TABLE 24. COMPOSITION OF SIMULATED DELAWARE RIVER WATER

Compound	Conc (μMolar)	Conc (mg/L)
$MgCO_3$	30	2.53
Na_2CO_3	205	21.74
K_2CO_3	32	4.42
$CaCO_3$	333	33.32
NH_4Cl	15	0.79
$CaCl_2$	120	13.32
$NaNO_3$	12.9	1.10
$MgSO_4$	220	26.47
$NH_4(SO_4)_2Fe$	22	5.84
H_3PO_4	4.21	0.526
0.1N HCl	26.3	---

Sufficient 0.1N NaOH to adjust final pH to 7.3.

Based on 10 year average values(162)

Section 7

RESULTS

OZONATION STUDIES - LABORATORY

The objective of the laboratory ozone study was to develop an understanding of the ozone process for drinking water. This included development of a laboratory protocol which could be used to observe the effect of ozone treatment prior to its incorporation into a large scale operation. The specific ozone studies include:

1) Ozonation of Delaware River water
2) Ozone utilized
3) Ozonation kinetics

Ozonation of Delaware River Water

The ozonation of Delaware River water was carried out in three phases:

1. A screening phase to determine what water quality parameters important;
2. a second phase to investigate detailed effects of ozone on selected water quality parameters; and
3. a final phase for the monitoring of changes in selected parameters under optimum ozonation conditions.

Screening Phase for Torresdale Waters --
Screening experiments were performed to enable selection of analytical techniques with which to follow the course of ozonation of Torresdale waters and also to judge the impact of ozone on the water. In these experiments, water was ozonated at two contact times of 10 and 20 minutes, and two ozone doses of 1 and 3 mg/L in addition to being oxygenated. Untreated Delaware River water (Site 1), and the influent and effluent of the Torresdale Plant RSFs or (Sites 4 and 5, respectively) were ozonated to see the impact of pretreatment on the ozonation process. This work led to the ozone conditions used for the pilot-scale study and its analysis.

A typical analysis of the Delaware River water used for the laboratory investigations is shown in Table 25. Additionally, Delaware River ultrafilter retentate (UM10 membrane) with the fraction of molecular weight greater than 1000 (nominal) concentrated 10 times was used.

Experiments were performed on disinfection, oxidation of THM precursors, TOC and UV absorbance at 254 nm (A254) to ascertain which of these would be a usable technique for monitoring the course of ozonation. It was found that ozone doses as small as 1 mg/L for a contact time of 10 minutes were sufficient to disinfect Delaware River water, as indicated by standard plate counts (103) (see Table 26). The results of the disinfection experiments indicate that there is no substantial difference in the degree of bacterial disinfection resulting from the application of 1 or 3 mg/L ozone applied dose, or between 10 and 20 minute contact times. At the 1 mg/L dose, however, there were large amounts of mycelia on the plates, indicating that higher doses are necessary to inactivate fungi. Chlorinated process water was found to contain no bacteria on examination by SPC techniques, so the effect of ozone disinfection could not be determined.

TABLE 25. TYPICAL ANALYSIS OF DELAWARE RIVER WATER USED FOR OZONE TESTING

Parameter	Delaware River	Analysis Reference
pH	7.4	103
Turbidity (NTU)	2.6	103
Color (A420)	not detected	103
A254	0.62	
TOC (mg/L)	2.5	
Carbonyl Concentration (μeq C=O/L)	not detected	Dinitrophenylhydrazine Test (154)
Phenolics (gallic acid equivalents, GAE)	2.6	Folins Test (155)
Color		
dominant λ (nm)	560	
purity	10%	
hue	greenish-yellow	
THMFP ($\mu g CHCl_3/L$)	200	(See Experimental Section)
Total iron (mg/L)	1.2	103
Manganese (mg/L)	0.20	103

It was concluded from these results that disinfection is likely to be accomplished under any dose, residual, or contact time that may be considered for the Pilot Plant experiments. This conclusion is supported by the work of other researchers who found that extremely short contact times (156) and small ozone doses (157) were adequate to effect ozone disinfection of water.

The effects of ozone on THMFP were found to be ambiguous (Table 27). In some cases, THMFP was decreased by application of ozone, in others it increased, and in still others, there was no change. There was no correlation between ozone dose or contact time and THMFP. The literature on the effect of ozone on formation of THMs has recently been reviewed by Umphries and coworkers (158) and by Rice (159). They found that there was a wide range of reduction of THM precursors by ozonation and, in several cases, an increase. An explanation for this phenomenon may be a result of ozone operating through different mechanisms in different cases as proposed by Hoigne (58).

In all cases, TOC was reduced by ozonation. The degree of removal was contact time and ozone dose dependent. Raw water TOC was reduced to a greater degree than TOC of water that had been treated (Table 28). TOC is thus concluded to be a useful parameter for monitoring the course of ozonation. Draw-

TABLE 26. DISINFECTION OF DELAWARE RIVER WATER

O_3 Dose mg/L	Plate counts (CFU/mL)		
	Untreated	10 min O_3	20 min O_3
1	2400 ± 420	43 ± 4.2	31 ± 1.3
3	2800 ± 600	1.7 ± 1.2	0.33 ± 0.58
3	4200 ± 600	44 ± 23	21 ± 5

TABLE 27. CHANGE OF THMFP VALUES ON OZONATION OF DELAWARE RIVER WATER

Treatment	THMFP (ug/L)		
	RSF(TP)*	CLAR(TP)*	RIVER*
oxygen	291 ± 15	559 ± 101	420 ± 37
1mg/L O_3,10 min	162 ± 14	571 ± 97	452 ± 15
1mg/L O_3,20 min	148 ± 14	580 ± 91	467 ± 28
oxygen	321 ± 12	434 ± 20	512 ± 24
3mg/L O_3,10 min	231 ± 12	268 ± 24	434 ± 3
3mg/L O_3,20 min	185 ± 25	286 ± 25	409 ± 9

*See Table 4 for explanation of nmemonic

Note: Experiments with 1 and 3 mg/L doses were conducted on different water samples and are not directly comparable.

TABLE 28. PERCENT TOC LOST UPON OZONATION OF DELAWARE RIVER WATER

Treatment	RSF(TP)	CLAR(TP)	RIVER
oxygen	0%	24%	4%
1mg/L O_3,10 min	0	14	11
1mg/L O_3,20 min	7	19	20
3mg/L O_3,10 min	10	19	24
3mg/L O_3,20 min	21	27	30

See note, Table 27.

backs to this technique are related to the expense and complexity of the necessary equipment and the difficulty in automating the procedure.

A254 was also reduced uniformly by ozonation (Table 29). The rate of A254 removal was found to be dependent on contact time but not on ozone applied dose. As in the case of TOC, the effect was greatest on raw as compared to treated water. In contrast to TOC, the percentage removals were very large. This greater degree of discrimination coupled with the cost effectiveness of monitoring equipment give the UV technique a decided edge over TOC as an in-plant monitoring technique. It should be kept in mind, however, that a degree of caution should be exercised in interpreting UV absorbance results to follow the course of ozonation of natural humic materials. UV absorbance is a function of both the concentration and type of chemical species present and, without further characterization, cannot be used to completely delineate a chemical system.

TABLE 29. PERCENT A254 LOST UPON OZONATION OF DELAWARE RIVER WATER

Treatment	RSF(TP)	CLAR(TP)	RIVER
oxygen	0%	23%	28%
1mg/L O_3,10 min	33	54	70
1mg/L O_3,20 min	38	62	80
3mg/L O_3,10 min	29	54	72
3mg/L O_3,20 min	60	69	80

See note, Table 27.

The use of this initial screening information in conjunction with the breakpoint (t_1) concept discussed below led to a set of standard laboratory conditions for the ozonation of Delaware River water (Table 30). The second phase of experiments was then carried out under these conditions.

Effect of Ozonation on Other Water Quality Parameters --

The effects of ozone on several water quality parameters under the standard conditions were also investigated over a period of several months. The results of this study are shown in Table 31. Ozonation has a minimal

TABLE 30. STANDARD CONDITIONS FOR THE OZONATION OF DELAWARE WATER (160)

Ozone generator	Welsbach T408
Water sample volume	650 mL
contact time	15 min
monitoring	254 nm
ozone dose	3 mg/L
gas flow	0.5 SLPM
ozonator voltage	60 V AC
contactor k_La	1.72 min^{-1}

V = volts
k_La = mass transfer coefficient

effect on most water quality parameters under the standard conditions. With respect to these results, it is to be expected that dissolved oxygen would increase as the water is being aerated in the ozonation process. Additionally, the end product of ozone decomposition in water is oxygen. The variable effect on pH is possibly due to sparging of carbon dioxide rather than ozonation. The lack of effect on turbidity is correlated with the lack of effect on iron. If the iron is in a ferrous, soluble form, it may be oxidized to a ferric, insoluble form by ozone (161). This would result in formation of a precipitate with a consequent increase in turbidity. If the iron is already oxidized and insoluble, there will be no change in turbidity from this source. Analysis of Delaware River water indicates that only a small proportion of the iron is soluble (162). With respect to other compounds, ozone should have no effect on nitrogen speciation when ammonia is in the protonated form (62). Since the pK_a of ammonia is much greater than the pH of the water, there is insufficient ammonia present to be oxidized to nitrate by ozone. Other relationships between ozone and the matrix are discussed in Appendix E.

Optimizing Ozonation of Organics --

Organic parameters were all affected by ozonation. TOC, A254, and phenolics were removed whereas carbonyl compounds including glyoxylic acid were increased. This is consistent with organic reactions with ozone as noted in the literature (66).

Additional work was then carried out to follow the reaction of ozone with organics as a function of time. A typical result is shown in Figure 26 for DOC in Delaware River ultrafilter retentate. The effects of ozone on carboxylic acids, carbonyl compounds (154) and LMW aldehydes (glyoxylate) (163) are somewhat more variable than DOC. It is evident from the results, however, that these materials are being formed on ozonation as has been described in the literature (66,67,74,76,77).

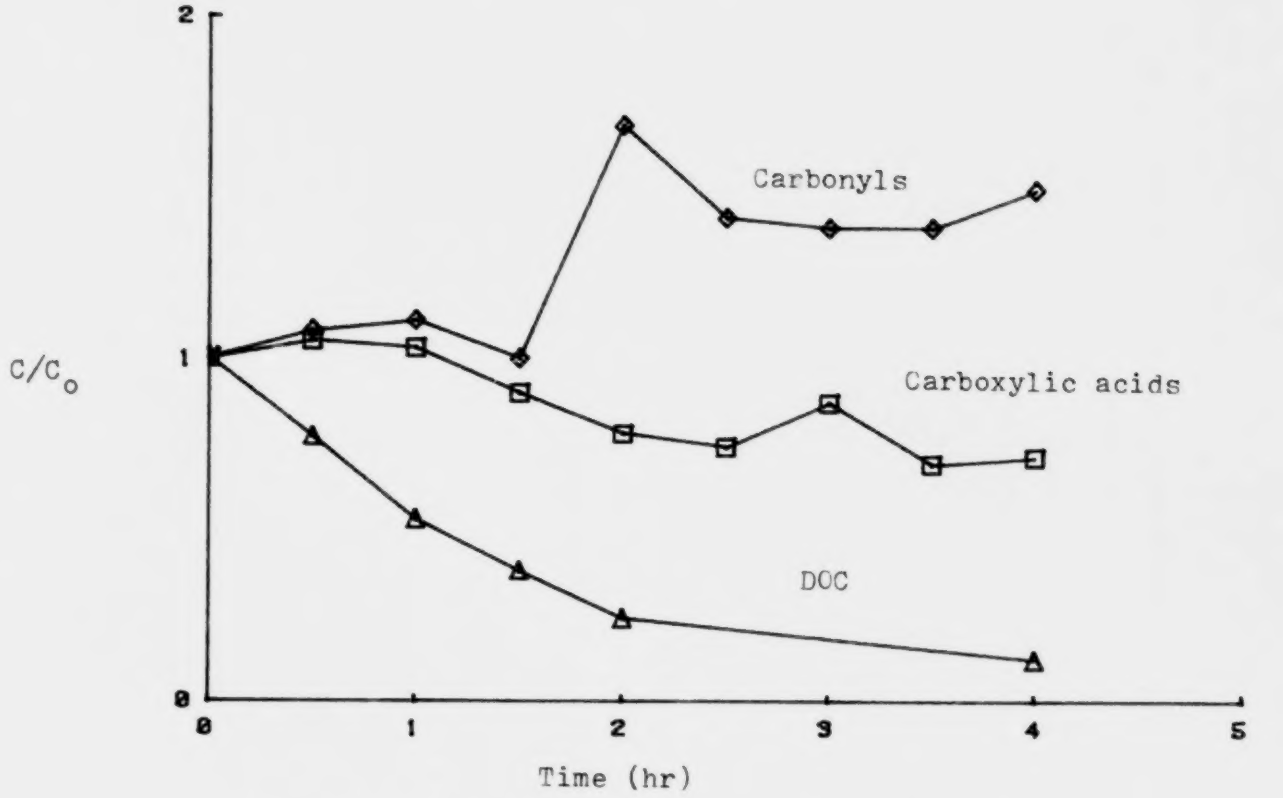


Figure 26. Ozonation of Delaware River Ultrafilter Retentate.

TABLE 31. EFFECT OF OZONE ON WATER QUALITY OF DELAWARE RIVER WATER

Parameter	Representative Value	Effect of Ozone
A. Water Quality Parameters		
pH	7.3	±
conductivity	1 mmho	none
alkalinity	30 mg/L as $CaCO_3$	none
turbidity	21 NTU	none
dissolved oxygen	8.6 mg/L	+
B. Inorganics		
Nitrite	0.056 mg/L	none
Nitrate	0.8 mg/L	none
Ammonia	0.65 mg/L	none
Phosphate	0.04 mg/L	none
Iron	0.14 mg/L	±*
Manganese	0.02 mg/L	none
C. Organics		
TOC	3.5 mg/L	−
Phenolics (155)	1.3×10^{-5} GAE	−
Carbonyls (154)	Concentrates only	+
A254 (10 cm cell)	0.5	−
Aldehydes of Low Molecular Weight (e.g. glyoxylic acid) (163)	Concentrates only	+

*depends on solubility

− = decreases

+ = increases

± = variable

Product formation was investigated in greater detail by ozonation of some models and analogs of natural humic materials. With respect to humic acid, the amount of carbonyl compounds formed shows two maxima (Figure 27). A precipitate was observed at the first maximum. If these points are removed from the plot, it appears that carbonyl formation undergoes a continuous and moderate increase throughout the experiment. At the same time A420 undergoes a continuous removal.

In the case of a model compound which contains hydroxy aromatic groups (catechin) but also reacts with dinitrophenylhydrazine, the carbonyl type functionality is oxidized along with the phenolic (Figure 28). If the functional group plots are compared to the A254 plots, it appears that the material undergoes a strong degree of what is possibly oxidative coupling throughout the experiment (202).

The last phase of the investigation of the ozonation of Delaware River consisted of creating ozonation conditions designed to produce optimum results. Rather than the standard conditions (Table 30), samples were ozonated under the following conditions (Table 32).

TABLE 32. HIGH DOSE AND MASS TRANSFER CONDITIONS FOR THE OZONATION OF DELAWARE RIVER WATER

Ozonator Generator	Welsbach T408
Sample size	2.0 L
Ozonator	75 V AC
Gas flow	2.0 SLPM
Ozone dose	3.8 mg/L
Contactor k_La	7.8 min^{-1}
Contact times	15 min = A254 breakpoint 45 min = A254 exhaustion

It should be noted that the increase in k_La and dose should act to accelerate the reaction over standard conditions. A comparison of the two conditions (standard vs. optimized) indicates that considerably more ozone is consumed under the new conditions. The results of the experiments are shown in Table 33. It is interesting to note that many of the organic parameters associated with the Delaware River increased on ozonation. A similar phenomenon may be observed if the absorbance at 254 nm of Delaware River water is followed on ozonation well past the breakpoint (Figure 29). Polymerization processes appear to be occurring when ozone is applied for long periods of time. Subsequently as shown on Figure 29, the organic polymers are broken down. This data indicates extreme care should be exercised when defining the ozone process as it is clearly time dependent. The evidence for polymerization (oxidative coupling) and depolymerization (oxidative degradation) of organic materials has been derived from experimentation with model compounds in an investigation which parallels this project (202).

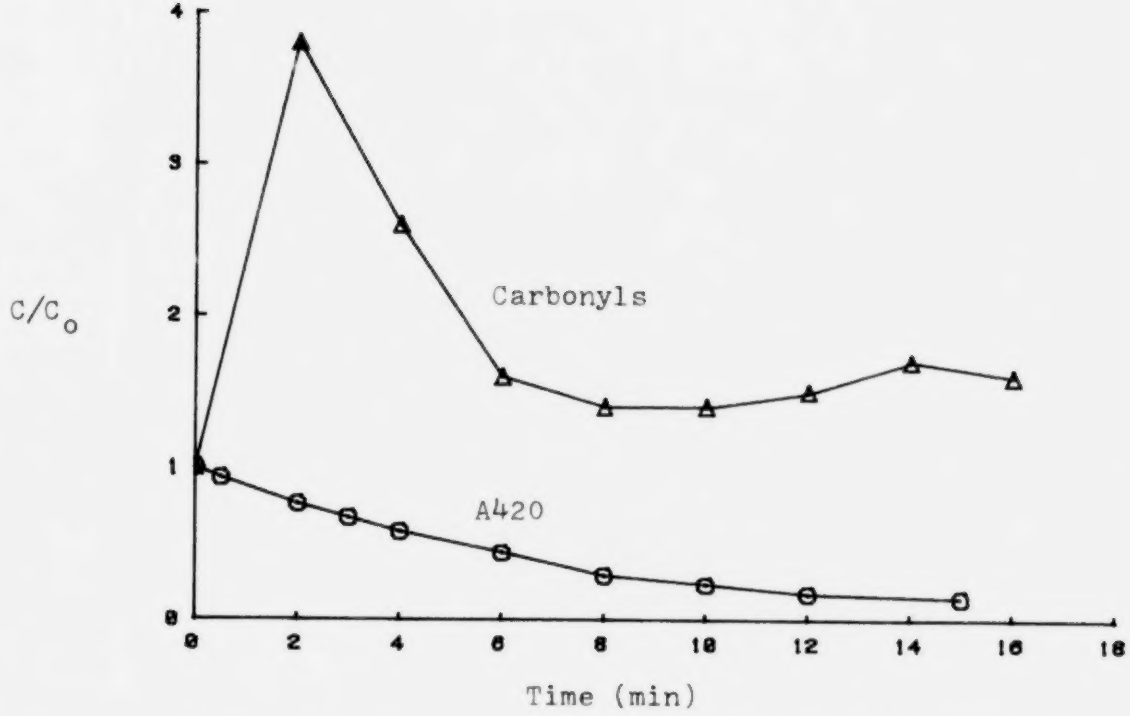


Figure 27, Products of Ozone Reaction with Humic Acid.

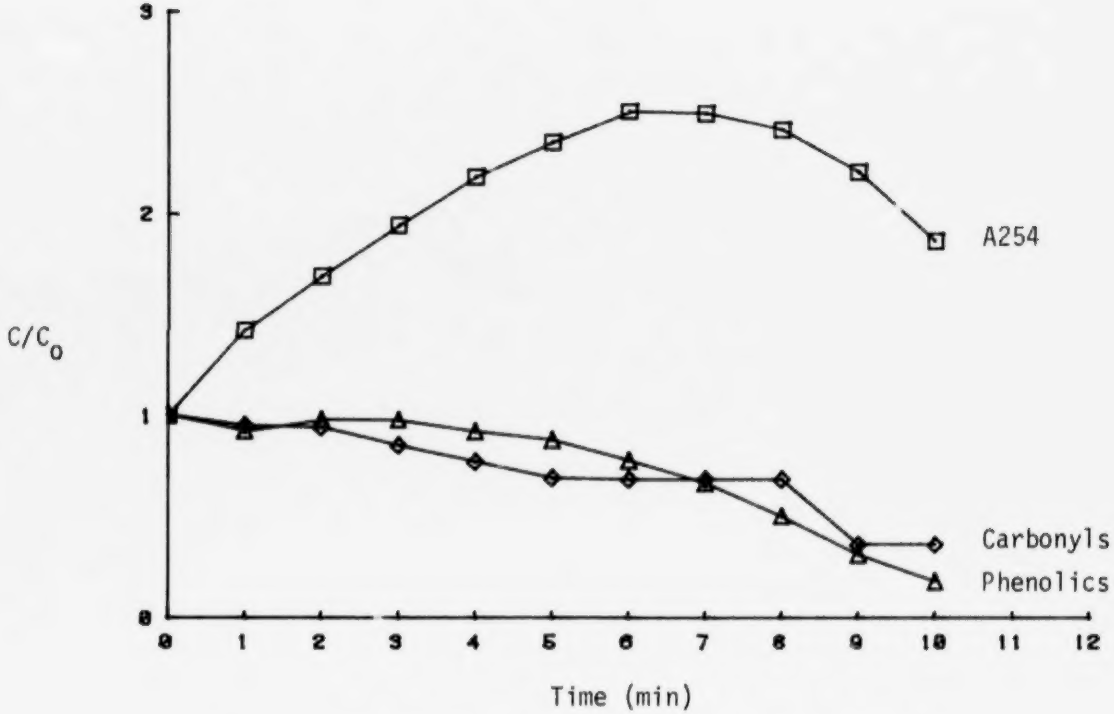


Figure 28. Ozonation of Catechin.

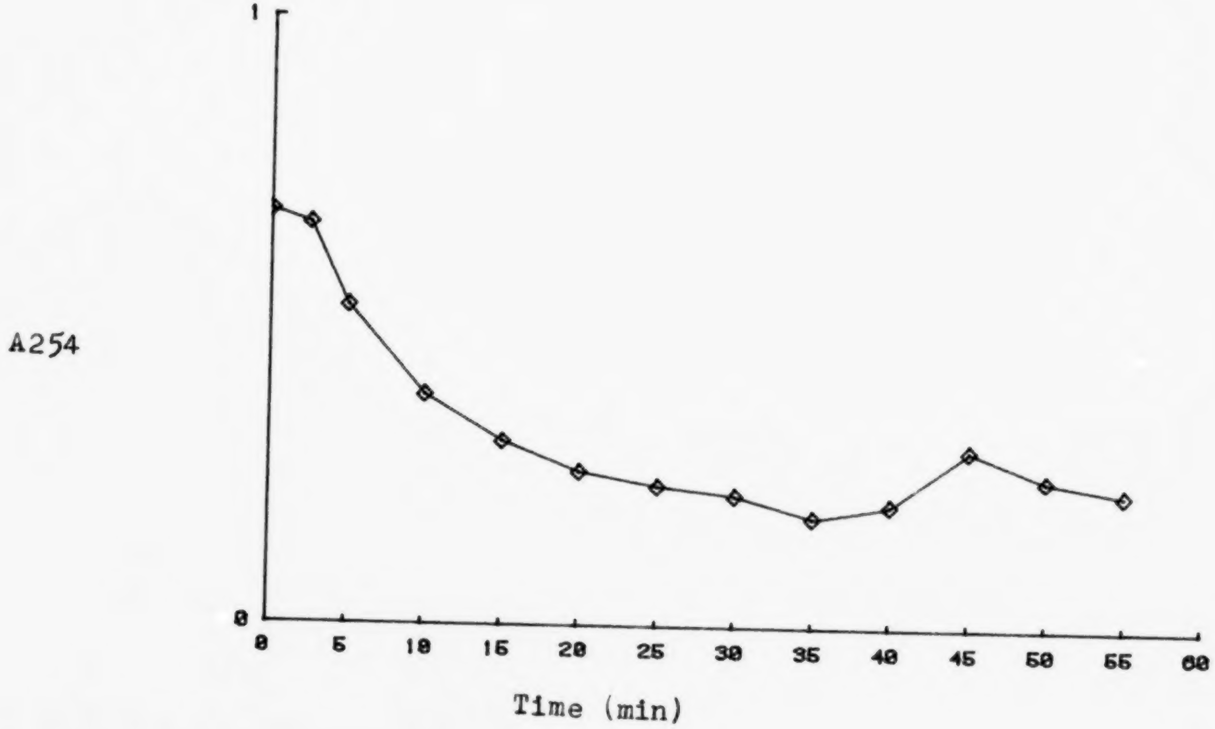


Figure 29. Ozonation of Delaware River Water.

TABLE 33. OZONATION OF DELAWARE RIVER WATER

Parameter	Unozonated	Breakpoint Ozonation (15 min)	Exhaustive Ozonation (45 min)
pH	6.1	7.4	6.7
Turbidity (NTU)	2.6	7.8	8.6
Phenolics (GAE)	2.6	ND*	6.2
Carbonyl's (ueq C=O/L)	ND	ND	ND
A420	ND	ND	ND
A254	0.301	0.083	0.119
TOC (mg/L)	2.5	1.0	9.0
THMFP (ug $CHCl_3$/L)	190	280	280

Experimental conditions shown in Table 32

* ND = not detected

Ozone Utilized

Experimentally, ozone utilized is a simple mass balance with respect to ozone. In a typical experiment, the ozone applied dose is first measured. Following this, a measured volume of water or a solution of substrate is ozonated for a specified amount of time. The off gases from the ozone contactor are passed through a Greenberg-Smith impinger containing approximately 500 ml of 2% KI and a safety trap containing about 25 ml of 2% KI (103). After impingers, the off gases are measured volumetrically with a wet test meter. The residual in the solution is measured by the modified IDS technique (see Experimental). After application of appropriate correction factors, the ozone utilized is calculated as:

$$OU = \frac{(O_{3in} - O_{3out})V_{gas}}{V_{liq}} - O_{3res}$$

where: O_{3in} = applied dose, mg/L
O_{3out} = amount of ozone in the off gases, mg/L
V_{gas} = volume of gas (ozone and oxygen) applied in L at STP
V_{liq} = volume of liquid in contactor, L
O_{3res} = ozone residual in the contactor, mg/L
OU = ozone utilized, mg/L

The ozone utilized experiment is usually run in triplicate and the results averaged. If there is a great deal of variability, further trials are conducted.

It may be noted that there is a great deal of variability in the ozone utilized (OU) measurements. At times, the coefficient of variation of a series of measurements may reach several hundred percent. This is a result of both inherent error in the experiment and also the mathematical propogation of error in the OU function.

In a derived function, the possible error in the dependent variable (OU) is related to the independent variables (O_{3in}, O_{3out}, O_{3res}) by the sum of the absolute values of the products of the error of the independent variables and their differentials with respect to the dependent variable. If the gas and liquid volumes are held constant, the above equation may be rewritten as follows:

$$OU = (O_{3in})V - (O_{3out})V - O_{3res}$$

where $V = V_{gas}/V_{liq}$
The possible error is:

$$\Delta OU = \left| \frac{\partial OU}{\partial O_{3in}} \times \Delta O_{3in} \right| + \left| \frac{\partial OU}{\partial O_{3out}} \times \Delta O_{3out} \right| + \left| \frac{\partial OU}{\partial O_{3res}} \times \Delta O_{3res} \right|$$

where Δ represents the error in a variable and the negative signs have been made positive to account for the absolute values. Performing the indicated differentiation:

$$\Delta OU = V\Delta O_{3in} + V\Delta O_{3out} + \Delta O_{3res}$$
$$\text{or } \Delta OU = (\Delta O_{3in} + \Delta O_{3out})V + \Delta O_{3res}$$

The net result of this error analysis is that even if the errors in the individual parameters (O_{3in}, O_{3out}, O_{3res}) are minimized, the overall value will be controlled by V. In a typical experiment, V_{gas} = 7.0 L, and V_{liq} = 0.65 L, thus V = 10.8. If there is an acceptable 5% error in the measured parameters, typical values could be:

O_{3in} = 4 mg/L　　ΔO_{3in} = 0.2

O_{3out} = 3 mg/L　　ΔO_{3out} = 0.15

O_{3res} = 1 mg/L　　ΔO_{3res} = 0.1

$$OU = (4-3)(10.8) - 1 = 9.8 \text{ mg/L}$$
$$\Delta OU = (0.2 + 0.15)(10.8) + 0.1 = 3.9 \text{ mg/L}$$
$$\text{or } OU = 9.8 \pm 3.9 \text{ mg/L}$$

a coefficient of variation of 40%.

Thus, to minimize the overall error, it is important to:

1. maintain constant volumes
2. minimize individual errors
3. minimize volume ratios
4. perform several replicates

In the pilot scale operations, smaller volume ratios would indicate the smaller error. A typical value of V in the pilot plant was 4.8 (see Table 5). A coefficient of variation of 18% results if this value is used in the above equations. This indicates that there will be a considerably greater precision in the pilot scale compared to the laboratory scale due to error propagation as a consequence of the physical dimension of the apparatus used. This prediction has been verified by experiment. For the pilot plant contactor, ozone utilized tests prior to start-up revealed an ozone utilized average value of 0.80 ± 0.20mg/L (CV = 25%); for the Torresdale contactor, 2.44 ± 0.44mg/L (CV = 18%).

As mentioned previously, ozone utilized was to be used as a measure of the ozone demand of a system or as a measure of the stoichiometry of the reaction of ozone with different substrates. To test the applicability of ozone utilized in these situations, a series of experiments were conducted. These experiments investigated interference by chlorine, the effect of ozone applied dose, pH effect, buffer composition effect, and the effect of substrate concentration.

Chlorine is thought to be an interference in the KI measurement technique. Chlorine gas can react with KI and additionally it is volatile, therefore it may be stripped out of the reaction solution and captured in the post contactor KI trap. To test this, a solution of water containing chlorine (1.6 mg/l free chlorine by the DPD method (103)) was placed in the contactor and the ozone utilized determined. Following this, the procedure was blanked by substituting oxygen for ozone and repeating the experiments. As anticipated, chlorine was stripped and, after calculation, was found to account for approximately 2% of the KI oxidized. Therefore, if solutions already containing an oxidant are to be ozonated for ozone utilized measurements, an oxygen blank should be run and the results subtracted. Blanks show that oxygen alone does not react with KI.

The effect of ozone applied dose on ozone utilized was studied at pH 3 and pH 8. The results are shown on Figure 30 where each data point represents the average of at least three ozone utilized values. These experiments indicate that at high ozone doses, there is an increased ozone utilized. The reason for this is not immediately apparent. This potential problem is circumvented in subsequent measurements by using ozone applied doses of less than 5 mg/L.

The rate of ozone decomposition is strongly affected by pH (101) as is the speciation of ozone in aquatic solution (61). It was decided, therefore, to investigate the effect of pH on ozone utilized by determining the ozone utilized in a series of phosphate buffers of constant ionic strength. The results are shown in Table 34. There was found to be no statistically significant interaction between pH and ozone utilized at the $p < 0.05$ level. This result is confirmed by inspection of pH and ozone utilized data from the pilot plant.

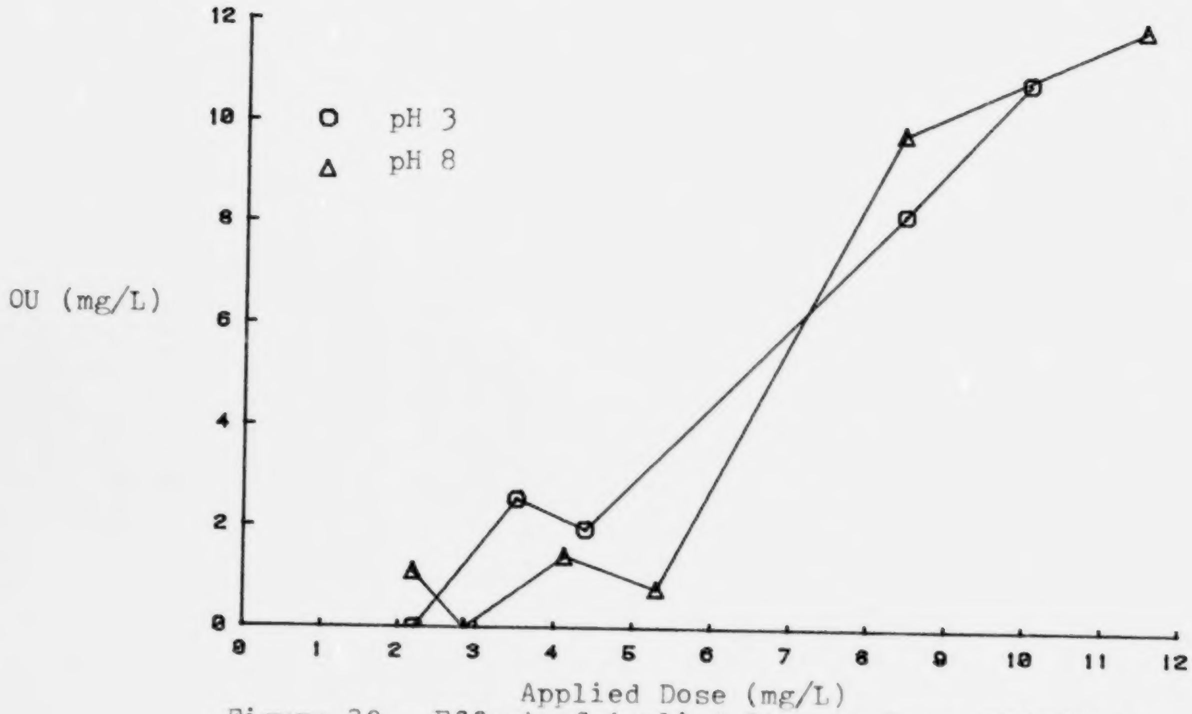


Figure 30. Effect of Applied Dose on Ozone Utilized (Note that the dependence depicted at greater than 5 is due to poor efficiency at high dose rather than OU itself)

TABLE 34. pH EFFECT ON OZONE UTILIZED

pH (0.2 M PO_4^{-3} Buffer)	OU (mg/L)(mean ± SD)
4.2	2.38 ± 2.81
6	6.75 ± 6.35
8	1.01 ± 2.18
9	3.71 ± 1.93

Several studies were performed to investigate the effects of buffer strength and composition on ozone utilized. In these experiments, phosphate and carbonate buffers and perchlorate and chloride pseudo buffers were used. Cations in all cases were sodium and potassium. The results are shown in Table 35.

TABLE 35. BUFFER EFFECT ON OZONE UTILIZED

Buffer	pH	Ionic Strength	Ozone Utilized, mg/L
PO_4^{-3}	9	0.2 M	3.71 ± 1.98
CO_3^{-2}			8.52 ± 5.28
HCl/KCl	2	0.2 M	2.06 ± 3.46
$HClO_4/KClO_4$			0.23 ± 0.74
PO_4^{-3}	8	0.1 M	-0.60 ± 3.66
		0.2 M	1.01 ± 2.18

Statistical comparisons of the various systems indicate that neither ionic strength nor buffer composition affect the amount of ozone utilized. The high value for CO_3^{-2} is because it is a known inhibitor (a free radical scavenger) (62).

Lastly, the effect of substrate concentration on ozone utilized was tested. In these investigations, humic acid concentrations of 5, 10, and 15 mg/L were ozonated at pH 8 in 0.2 M I.S. phosphate buffer at ozone applied doses of 3 - 4 mg/L. The results for pH 8 are shown in Figure 31. These results indicate that ozone utilized increased linearly with humic acid concentrations at pH 8. These results were confirmed using tannin and lignosulfonic acid where the organic concentration was taken as the ultraviolet absorbance at various wavelengths. The relationship between ozone utilized and organic concentration was confirmed in the pilot plant work (see Figures 173 and 174).

The results are summarized in Table 36. These results indicate that substrate concentration has a positive and linear effect on ozone utilized whereas other effects are negligible. Therefore ozone utilized can be used in measurements of ozone demand and stoichiometry of ozone reactions with orgainc substrates.

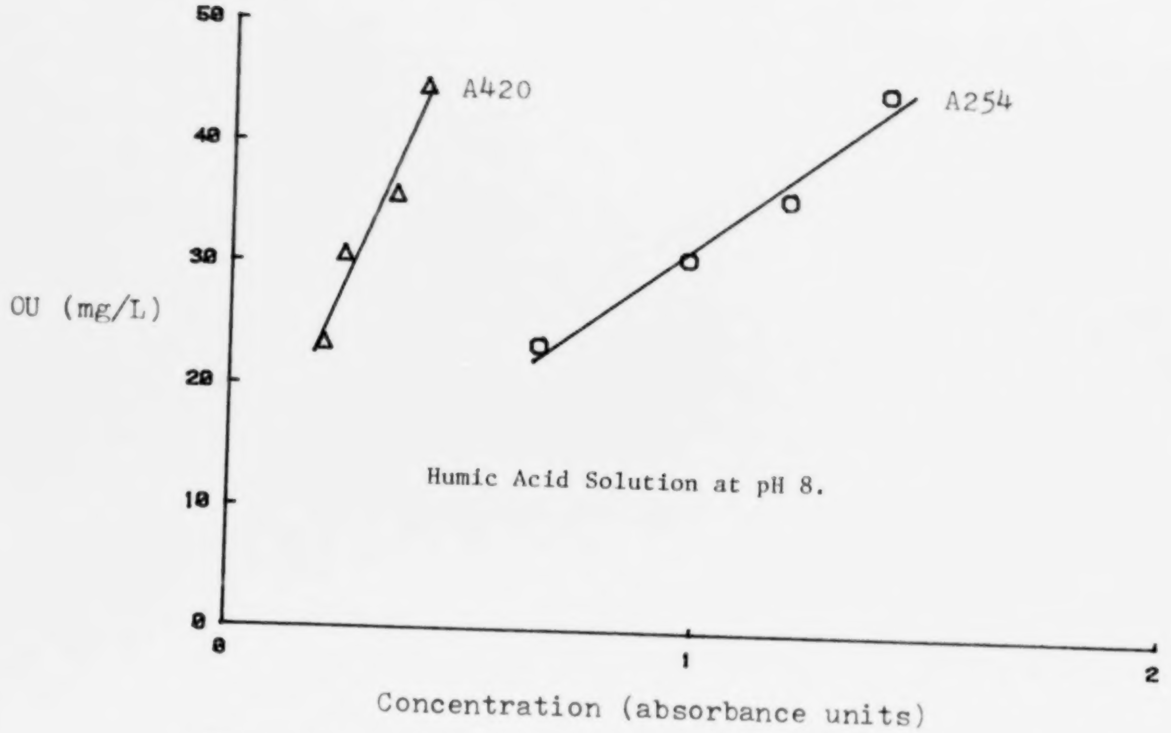


Figure 31. Ozone Utilized as a Function of Substrate Concentration

TABLE 36. SUMMARY OF OZONE UTILIZED PROPERTIES

Experiment	Anticipated Effect*	Found Effect
Buffer Strength	none	none
Buffer Composition	none, except for CO_3^{-2}	none, except for CO_3^{-2}
pH	none	none
Chlorine	interferes	interferes
Applied Dose	none	increases above 5ppm; none below 5ppm.
Substrate Concentration	increases	linearly increases

* Based on reference 105.

Ozone Kinetics

Decomposition of Ozone in Process Waters --

The rate of ozone decomposition was investigated in process waters at the Torresdale Water Treatment Plant and its associated Pilot Plant. Based on the literature (59) it was initially assumed that the decomposition reaction was first order with respect to ozone. The natural logarithm of the ozone residual was then plotted as a function of time after a sample had been saturated with ozone. That the reactions are indeed first order was confirmed by the coefficients of determination which were 0.98 for Pilot Plant and 0.99 for Torresdale Plant water. The results are summarized as follows:

Parameter	Pilot Plant	Torresdale
Order	1	1
k (min^{-1})	0.065	0.092
Half-life (min)	10.7	7.5
pH	6.56	7.55

Ozonation Kinetics of High Molecular Weight Organics --

Figures 32 and 33 show the effect on UV absorbance of ozonation of Delaware River water on humic materials concentrated from the water as a function of time. Both curves were completed at two different times under the standard operating conditions, Table 29. First, it is noted that the reaction rate of ozone and organics as represented by A254 follows first order kinetics with respect to UV absorbing organics.

The reaction appears to be independent of ozone applied dose or concentration as long as a large stoichiometric excess of ozone is maintained. Most significantly, the reaction may be represented by two, sequential, first-order rate curves (see Figure 26). Since the slope of the second curve is much lower than the first, it is likely that ozonating beyond this

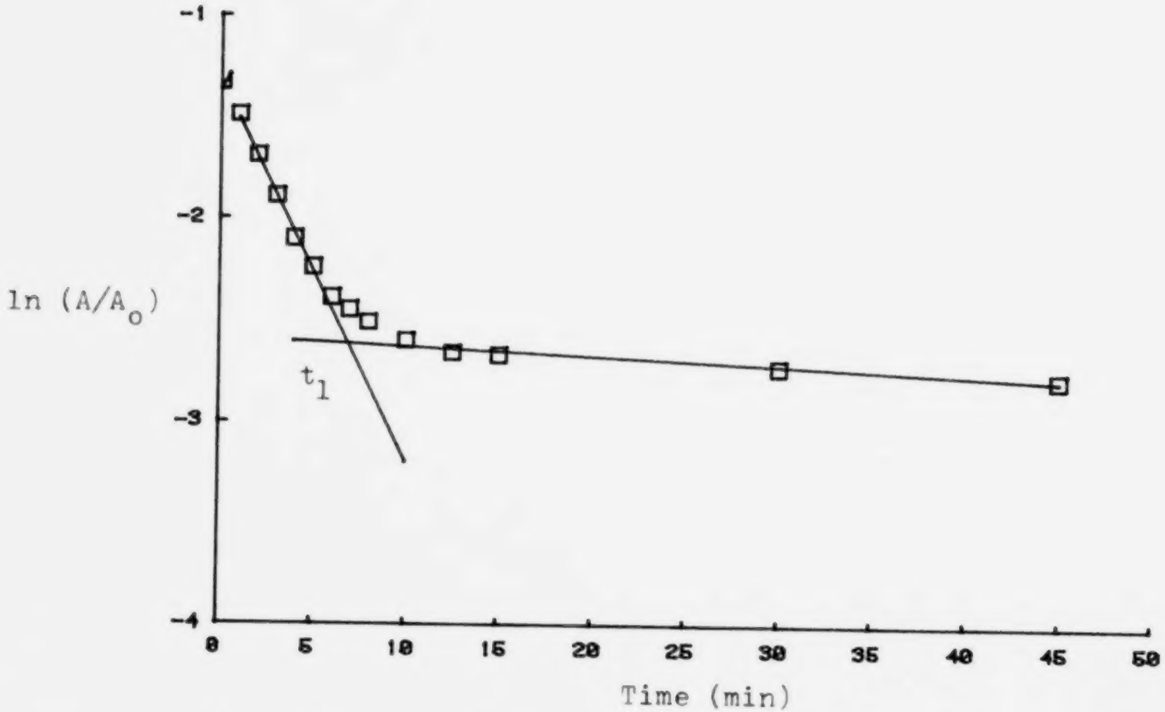


Figure 32. Breakpoint Ozonation I.

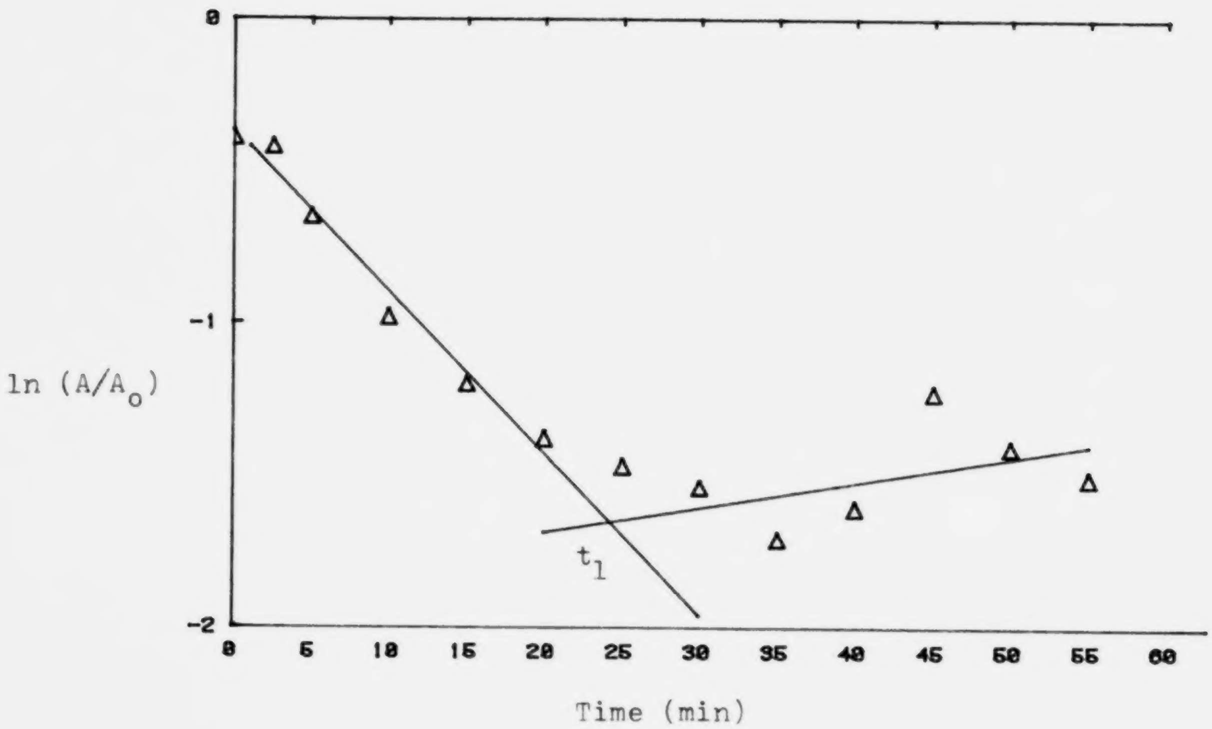


Figure 33. Breakpoint Ozonation II.

point in time will not yield results of a magnitude commensurate with that of energy input. The intersection of the two curves, designated as t_l, is a function of the nature and reactivity of the organic substrate measured as A254 (which is undergoing reaction), and it appears to be independent of ozone applied dose. Kinetic results for several systems may be seen in Table 37. The t_l values derived from these curves are considered to be the optimum contact times for this water, which are then taken to be the optimum hydraulic detention times of water in the ozone contactor in a continuous mode.

TABLE 37. SUBSTRATE KINETICS STUDIES

Source	A254(Initial)	O^3 Dose (mg/L)	t_l (min)	k (min^{-1})
UF Retentate*	0.745	6.6	35	0.04
	0.687	9.0	35	0.04
	1.56	3.4	35	0.04
Aldrich Humic Acid	7.25	7.1	17.2	0.12
Delaware River Water	0.46	4.1	10	0.08

*Delaware River ultrafilter retentate (UM10)

At this point, it is important to emphasize that the shape of the rate curve is at times ambiguous as a result of the complexity and variety of substrates present.

Breakpoint Ozonation - Another Kinetic Interpretation -- If the reactions of ozone and humic substances, as seen in Figures 32 and 33, are treated as second order with respect to substrate, only a slightly diminished goodness of statistical fit results. There is yet another model or interpretation to the data which has a good fit and possesses advantages which may be applied to the design of ozone processing equipment. In many cases, if the ozonation reaction is extended a sufficient amount of time and the natural logarithm of A254 plotted as a function of time, two straight intersecting lines result. This is indicative of two sequential first order processes. The slope of the second line may be of the same direction and lesser magnitude (Figure 32) or of opposite direction and lesser magnitude (Figure 33) than the first. If the two curves are subjected to linear regression analysis and the resulting two linear equations solved simultaneously, a time, t_l results. This time is termed the breakpoint for ozonation.

Since the second curve has a slope which is much less than that of the first, it is postulated that ozonating past this point will not yield results with respect to substrate removal which are commensurate in magnitude to the energy input to the process. The breakpoint is a function of the nature and reactivity of the substrate as measured by A254. It appears to be relatively independent of ozone applied dose although the data represents only a small range of doses. Results for several systems may be seen in Table 37.

A series of experiments were performed in order to trace the etiology of this phenomenom. First, it was hypothesized that ozone intially reacted with labile species and produced more oxidized and therefore more refractory species. If the breakpoint curve and a curve of some products are plotted on the same axis (Figure 34), the trends tend to support this hypothesis. Since glyoxylic acid is oxidized to oxalic acid and carbon dioxide by ozone, it is evident that the reaction should slow down once the majority of the glyoxilic acid has been consumed.

A second hypothesis would indicate an inhibition of the reaction by the production of acids which are products of ozonation. If the pH of the above reaction is followed as a function of time (Figure 35), there is a very strong inverse linear relationship between substrate concentration as A254 and acid concentration as pH ($r^2 = 0.979$). Other experiments have indicated that this reaction is sensitive to pH and increases in rate as pH increases. Thus, it is quite possible that the reaction may be inhibited by production of acid. It is most probable that both of the above mechanisms are operational.

Catalysis and Inibition -- Humic acid ozonation was conducted in the presence of several potential inhibitors or catalysts. Carbonate at $0.22\underline{M}$ concentration was chosen as an inhibitor due to the contention of Hoigne and Bader (62) that it acts as a free radical scavenger. Ferric chloride was chosen as a catalyst due to its role in free radical formation with Fenton's reagent (164). Chlorine and hydrogen peroxide were chosen for potential synergism with ozone, and Delaware River water was used to ascertain the effect of a complex matrix. The water in all these experiments was buffered at pH 8. The results may be seen in Table 38.

These results confirm the hypothesis that catalysis is impossible in the mass transfer limited situation. That carbonate is actually an inhibitor is not surprising due to Hoigne and Bader's work (62). This result has been confirmed for ozonation of a micropollutant (see below). Inhibition resulting from addition of hydrogen peroxide is probably due to the oxidation of peroxide by ozone. As controls, experiments were conducted on the chlorineoxygen system and the hydrogen peroxide-oxygen system. The hydrogen peroxide plus oxygen had no effect on humic acid. The chlorine system oxidized humic acid, but at a much slower rate than with ozone.

Aeration --

The passage of a large quantity of any gas through the ozone contactor could act to strip organics from solution. This is especially true in the case of volatile materials and those which are more soluble in air than in water. Since, in most cases, the non-specific parameters used only measure overall removal rates, it is often not immediately possible to distinguish between stripping (physical) or oxidative (chemical) removal. In order to assess the relative magnitude of the contribution of stripping to organics

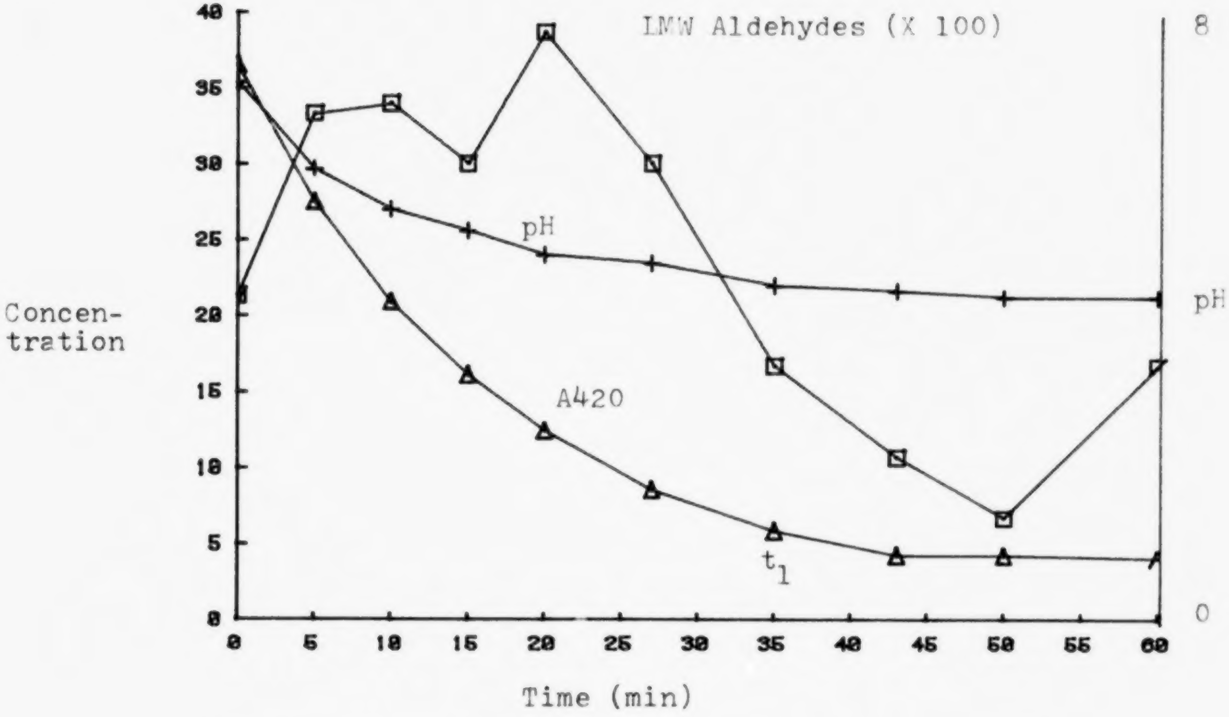


Figure 34. Relationship Between Products and t_1.

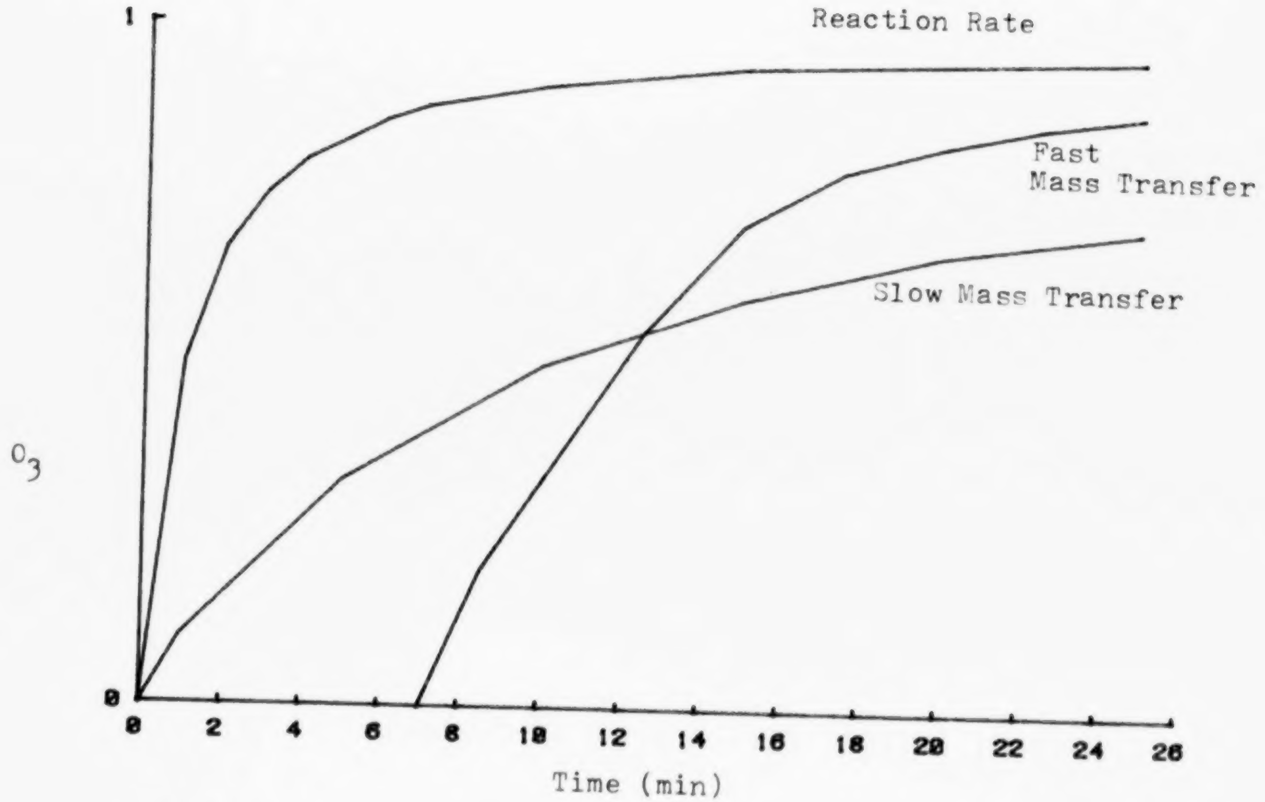


Figure 35. Theoretical Mechanisms of Ozone Uptake.

TABLE 38. EFFECT OF CATALYSIS AND INHIBITION

Additive	Normalized k_{obs} (min^{-1})	Effect*
Carbonate	0.0370 ± 0.0012	Inhibits
Del. River Water	0.0493 ± 0.0052	None
$FeCl_3$	0.0490 ± 0.0012	None
Cl_2	0.0624 ± 0.0052	None
H_2O_2	0.0244 ± 0.0009	Inhibits

*Based on t-test against baseline value of 0.0688 ± 0.0072

removal, a series of experiments was conducted. In the first experiment, a total of 60 L of oxygen was passed through 250 mL of Delaware River ultrafilter retentate with carbon parameters (total and inorganic carbon) measured before and after ozonation. The results indicated that 9.1% of the organic but none of the inorganic carbon was lost on ozonation. The ozonation of micropullants is evaluated in detail in Appendix E.

In order to investigate this further, a series of mass balances were conducted in which the off-gases from the ozone contactor were trapped and measured for carbon parameters. The results of two of these experiments are shown in Table 39. The variability in these experiments may be due to differences in the substrate (Delaware River ultrafilter retentate) or differences in ozonation parameters. In one of the experiments, both a base and a reducing (sodium thiosulfate) trap were employed. The fact that the base trap adsorbed 8% of the volatilized carbon indicated that acids were being trapped. It is highly likely that some low molecular weight volatile acids are being formed during the ozonation process and are subsequently stripped. In order to test this hypothesis, an experiment was conducted in which a measured amount of acetic acid (a suspected product of ozonation) was stripped in the ozone contactor and the concentration measured by titration before and after oxygenation. The conditions for oxygenation were essentially those of a typical ozonation experiment with the ozone generator unactivated. In this experiment, 15% of the acetic acid was transfered out of the ozone contactor by stripping, thus confirming the hypothesis.

In addition to the stripping of materials formed by the ozonation process, materials already in the water which may be refractory to ozonation can be stripped. If these compounds absorb light in the ultraviolet region, they would give the appearance of being lost on ozonation possibly confounding the results with respect to the humic substrate. An example of such a

TABLE 39. MASS BALANCES ON OZONATED PRODUCTS

Condition	Experiment I	Experiment II
Start	2.97 OC	2.64 OC
Left in ozonator after ozonation	0.68 OC 0.81 IC	2.22 OC
Trapped off gases during ozonation	0.82 OC 0.30 IC	0.32 OC
Unaccounted for	0.36 OC	0.11 OC
Total Stripped	28%	12%

OC = organic carbon, IC = inorganic carbon, all in mg/L

Substrate = Delaware River ultrafilter retentate at ambient pH and ionic strength

compound is p-dichlorobenzene. This material is volatile, absorbs in the ultraviolet, is refractory to ozone, and has been identified in the Delaware River (166). p-dichlorobenzene was investigated by ozonating and oxygenating and following the UV absorbance as a function of time. The first order rate constant for ozonation of this compound was found to be 0.102 ± 0.003 min^{-1} compared to 0.0980 ± 0.0004 min^{-1} for oxygen stripping. Although the rate constant for ozonation is statistically higher (t-test, a =0.05), it is not substantially so, and it is evident that air stripping plays an important role in the overall process. It is interesting to note that the rate limiting step for this reaction as determined by ozone uptake was found to be mass transfer of ozone although the compound is being stripped. During the experiment, no ozone was noted in solution for the entire procedure. This phenomenon is considered in detail as part of an ozone mass transfer model (Appendix D).

Determination of Rate Limiting Steps

The theoretical mechanisms of ozone uptake are presented in Figure 35. These mechanisms assume a stoichiometric excess of substrate. For the reaction rate controlled mechanism, ozone immediately appears in solution and quickly approaches the saturation concentration at a rate which approximates the k_La. In an ozone mass transfer limited reaction, no ozone appears in solution initially. With time ozone accumulates in solution at a rate which is greatly less then that predicted by the k_La. The third case, a quasi mass transfer reaction, is intermediate between the other two reaction mechanisms.

Rate limiting steps for the various substrates under consideration were separated into fast mass transfer, quasi mass transfer, and slow reaction rate

TABLE 40. RATE LIMITING STEPS

Substrate	pH	Fast Mass Transfer	Quasi Mass Transfer	Reaction Rate
Resorcinol	8	X		
	3	X		
Delaware River	7.4		X	
-HMW		X		
-LMW			X	
Lignin	3		X	
	8	X		
Tannin	3	X		
	8	X		
Camphor	8			X
Ellagic acid	8	X		
Gallic acid	3	X		
Coniferyl Alcohol	3		X	
	8	X		
Coumarin	3	X		
	8	X		
Catechin	3		X	
	8	X		
Diacetone-L sorbose	7			X
Humic acid	8	X		

limited by the methods of ozone uptake and reaction with dissolved ozone. The results are summarized in Table 40. Note that mass transfer plays an important role in most of the reactions studied in this investigation. Appendix D describes an ozone mass transfer model which was used in these studies. Appendix E presents a protocol for the ozonation of micropollutants which includes the aspects of ozone mass transfer and aeration.

In summary, it has been found that ozone reduces bacterial counts, TOC and A254 on the Delaware River. The effect on THMFP was variable. Experiments with humic, analogs, and model compounds indicate that the effects of ozonation on physical and inorganic water quality parameters are small, whereas there is a large effect on organics. These effects include reduction of TOC, A254, A420, phenolics and production of carbonyls, carboxylic acids and an oxidizing intermediate. Substrate reactions, kinetics of high and low molecular weight organics, aeration effects and analysis of the rate limiting steps of ozonation are defined.

PILOT SCALE STUDIES

The objective of the pilot studies was to determine the relative effectiveness of various advanced water treatment (AWT) systems in removing organic contaminants. Since this effectiveness is dependent upon the type and degree of pretreatment received, this section begins with a comparison of the Torresdale and Pilot Plant conventional treatment processes. This is followed by the results obtained from the operation of the ozone and ozone/sand processes. Lastly, the adsorption system results are presented.

In order to enhance the understanding of the data, four graphical techniques are utilized:

1) instantaneous concentration versus time graphs;
2) percent removal versus time graphs;
3) cumulative distribution function (CDF) curves; and
4) profiles of gas chromatograms.

The instantaneous concentration and percent removal graphs aid in visualizing actual organic levels in each system and their breakthrough characteristics. The percent removed (%R) is determined by the equation:

$$\%R = \frac{C_i - C_e}{C_i} \times 100$$

where C_i and C_e represent influent and effluent concentrations to the bed, respectively.

CDF curves delineate the percent of time that the data will fall at or below a given concentration. For example, if an effluent criterion of 100 ppb THMs is established for the Torresdale Plant rapid sand filter effluent, a CDF plot of the historical THM data will show the percent of time that this level has been achieved in the past. No hypothesis is made as to any underlying distribution function of the data and, as such, no predictions are made of future process performance. The curves were developed directly from the data and simply relate what had occurred.

Also presented are spiked profiles of chromatograms from broad spectrum gas chromatographic (GC) analyses. The spiked profiles characterize changes in the type and amount of a complement of organic compounds through a process or in a process with time. A broad spectrum of non-polar organic compounds with boiling points between 50° - 400°C and with 1-26 carbon atoms were isolated for this analysis using both the purge and trap technique and XAD macroreticular resin (MRR) compositors. Contingency tables and chi-square analyses were used to test the significance of any changes observed in the profiles.

Conventional Treatment

Table 41 presents a summary of the effectiveness of the Torresdale and Pilot Plant conventional treatment processes in reducing dissolved organic

TABLE 41. COMPARISON OF CONVENTIONAL WATER TREATMENT PROCESSES FOR DOC,THMT, AND THMFP REMOVAL (4/80 - 4/81)

Site:	DOC		THMT		THMFP[3]	
	ppb	%Δ	ppb	%Δ	ppb	%Δ
Delaware River						
(1) River[1]	2930	—	187	--	182	--
Torresdale Plant						
(4) CLAR[1]	2510	14%	NA[4]	--	NA	--
(5) RSF[2]	2559	13%	199	-7%	99	46%
Pilot Plant						
(13) CLAR[1]	2038	30%	140	25%	135	26%
(14) RSF[2]	1826	38%	123	34%	119	35%

[1] Arithmetic average of 13, 28-day composites. Each composite consisted of 20 grab samples

[2] Weighted average of 52, 30-minute composite samples collected once per week.

[3] THMFP conditions: 2.5 mg/l free chlorine at pH = 8.5; 3 days at 25°C.

[4] NA = Not available

%Δ : Average percent change from river concentrations.

carbon (DOC), trihalomethane formation potential (THMFP) and terminal trihalomethanes (THMT) from the Delaware River water. Based on the DOC results, the conventional treatment processes of the Pilot Plant were more effective than the comparable Torresdale Plant processes for the overall removal of organic compounds. This conclusion may be drawn through inspection of Figure 36, which shows the cumulative distribution curves for DOC in the Delaware River and in the rapid sand filter effluents from the two plants. Figure 37 presents the DOC results in terms of instantaneous concentrations. For ease of sample accessibility, the Pilot Plant raw water basin effluent (Site 11) was the site used for the collection of the river samples. Site 11 is considered equivalent to the collection of a Delaware River sample (Site 1) since no chemical nor physical process (except initial settling, which should not interfere with DOC measurements) was yet applied to the water. It should also be noted that Figure 36 includes only the data collected from 6/14/80 to 4/14/81 since DOC samples from Site 11 were not collected prior to that time.

Instantaneous trihalomethane (THMI) production through the Torresdale and Pilot Plants is depicted in Figure 38. Since the Pilot Plant had no prechlorination there was no THMI production, and only the THMI initially found in the river was found in its rapid sand filter effluent. Figure 39 presents the THMI results in terms of their cumulative distribution functions. The Torresdale Plant rapid sand filter effluent exceeded the recommended drinking water standard of 100 μg/l, 42% of the time. As a comparison, with the exception of a two month period during the summer of 1980, THMI levels remained below 5 μg/l in both the Delaware River and Pilot Plant rapid sand filter effluent. During the summer of 1980, the THMI levels ranged from 10 to 53 μg/l. This may be due to either a spill event in the Delaware River or to the backflow of chlorine/THMs from the Torresdale intake to the nearby Pilot Plant intake.

THMT and THMFP levels were each reduced 35% through the Pilot Plant (Table 41). Since the Pilot Plant had no trihalomethane production, this entire precursor reduction is attributed to precursor removal through the conventional treatment processes. This is in direct contrast with the Torresdale Plant where, although formation potential was reduced 46%, there was no corresponding decrease in THMT, indicating that the precursor reduction was due to trihalomethane production and not to organic removal. THMT levels in the Torresdale and Pilot Plant rapid sand filter effluents are shown in Figure 40.

Table 42 lists the volatile organic data for the Torresdale and Pilot Plant rapid sand filter effluents. Fifteen priority pollutants are observed in this group. The range of concentrations observed indicate the variability of the influent concentrations to the advanced water treatment systems. As expected, the THMs predominate at Torresdale. In comparison, all of the other volatile organics analyzed were of relatively low concentration. The apparent differences in average volatile organic levels between the Torresdale and Pilot Plant systems may be due to a number of causes. For example, carbon tetrachloride, which was not typically found in the Delaware River or through the Pilot Plant, was found in the Torresdale Plant rapid sand filter effluent. The apparent source of this contaminant is the chlorine used by

TABLE 42. RESULTS OF VOLATILE ORGANIC ANALYSIS-PLANT EFFLUENTS

Halogenated	Rapid Sand Filter Effluent			
	Torresdale Plant		Pilot Plant	
	Ave.	Range	Ave.	Range
[P] Chloroform	73.0	20-163	4.3	0.3-43
[P] Dichlorobromomethane	21.0	3.3-41	1.0	<0.1-11
[P] Dibromochloromethane	5.5	0.7-14	0.3	<0.1-2.7
[P] Bromoform	0.3	<0.1-1.0	<0.1	<0.1-0.2
[P] Methylene Chloride	0.3	<0.1-1.3	0.3	<0.1-1.8
[P] 1,2-Dichloroethane	1.4	<0.1-15	1.2	<0.1-9.0
[P] 1,1,1-Trichloroethane	0.2	<0.1-0.6	0.2	<0.1-0.8
[P] Carbon Tetrachloride	1.0	<0.1-16	<0.1	<0.1-0.6
[P] 1,2-Dichloropropane	6.1	<0.1-24	4.5	0.2-19
[P] Trichloroethylene	0.4	<0.1-1.5	0.2	<0.1-0.7
[P] 1,1,2,2-Tetrachloroethylene	0.4	<0.1-1.6	0.4	<0.1-3.0
[P] Chlorobenzene	0.1	<0.1-2.4	<0.1	<0.1-1.3
Bis(2-Chloroethyl) Ether	<0.3	<0.3	<0.3	<0.3
1,2-Dichlorobenzene	<0.1	<0.1	<0.1	<0.1

Non-Halogenated	Rapid Sand Filter Effluent			
	Torresdale Plant		Pilot Plant	
	Ave.	Range	Ave.	Range
Acetone	14.2	1.1-72	7.3	<0.3-63
Dimethoxymethane	3.7	0.3-17	4.1	<0.3-19
[P] Benzene	0.2	<0.1-0.8	0.2	<0.1-0.7
[P] Toluene	0.5	<0.1-5.1	<0.1	<0.1-1.0
[P] Ethyl Benzene	<0.1	<0.1-0.5	<0.1	<0.1-0.6
Cumene	0.2	<0.1-1.3	<0.1	<0.1-1.6
o-Xylene	0.1	<0.1-0.8	<0.1	<0.1-0.9
m-Xylene	0.1	<0.1-0.5	<0.1	<0.1-0.8

[P] - Priority Pollutant (11)

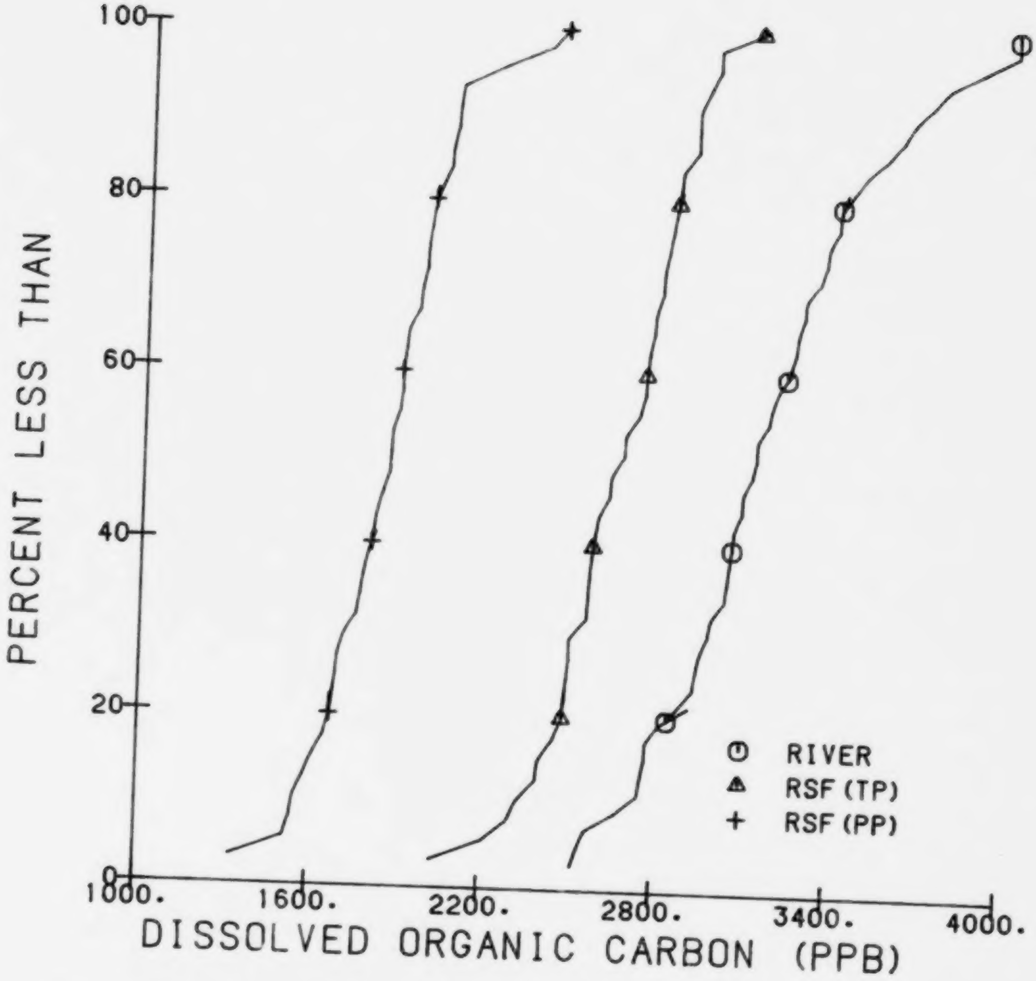


Figure 36. The effect of conventional treatment on DOC levels (6/80 to 4/81).

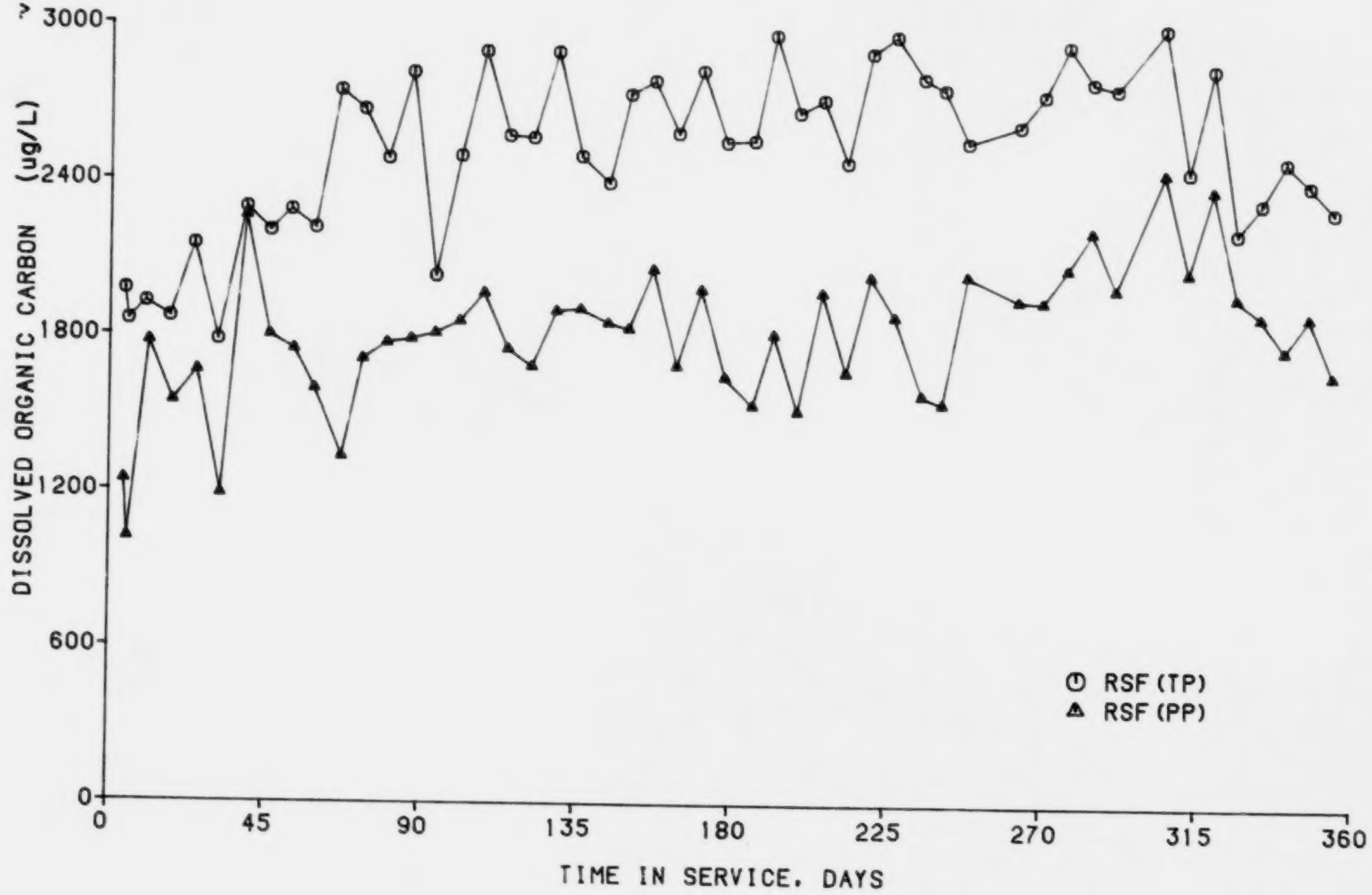


Figure 37. DOC levels in the rapid sand filter effluents.

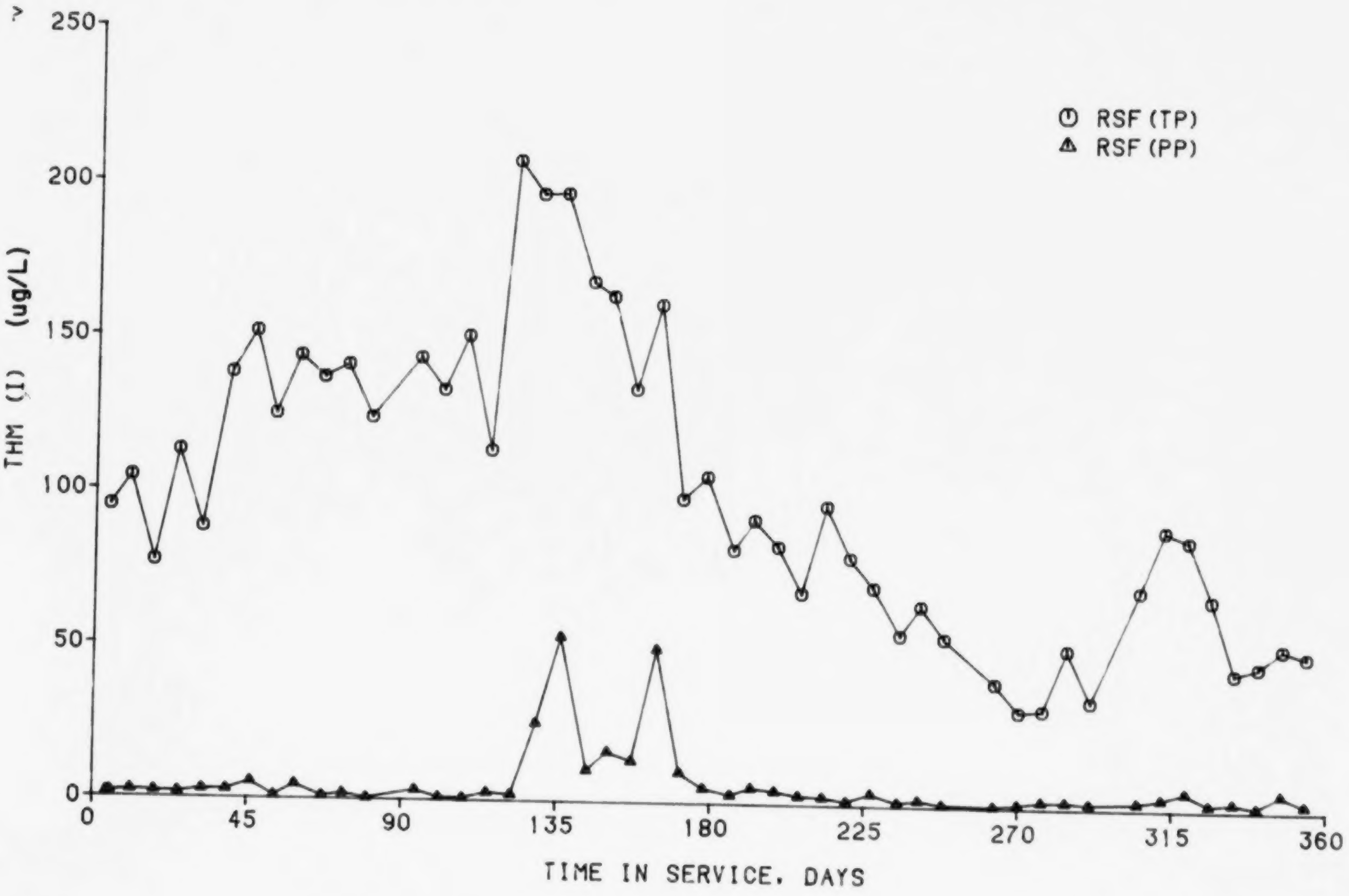


Figure 38. THM(I) levels in the rapid sand filter effluents.

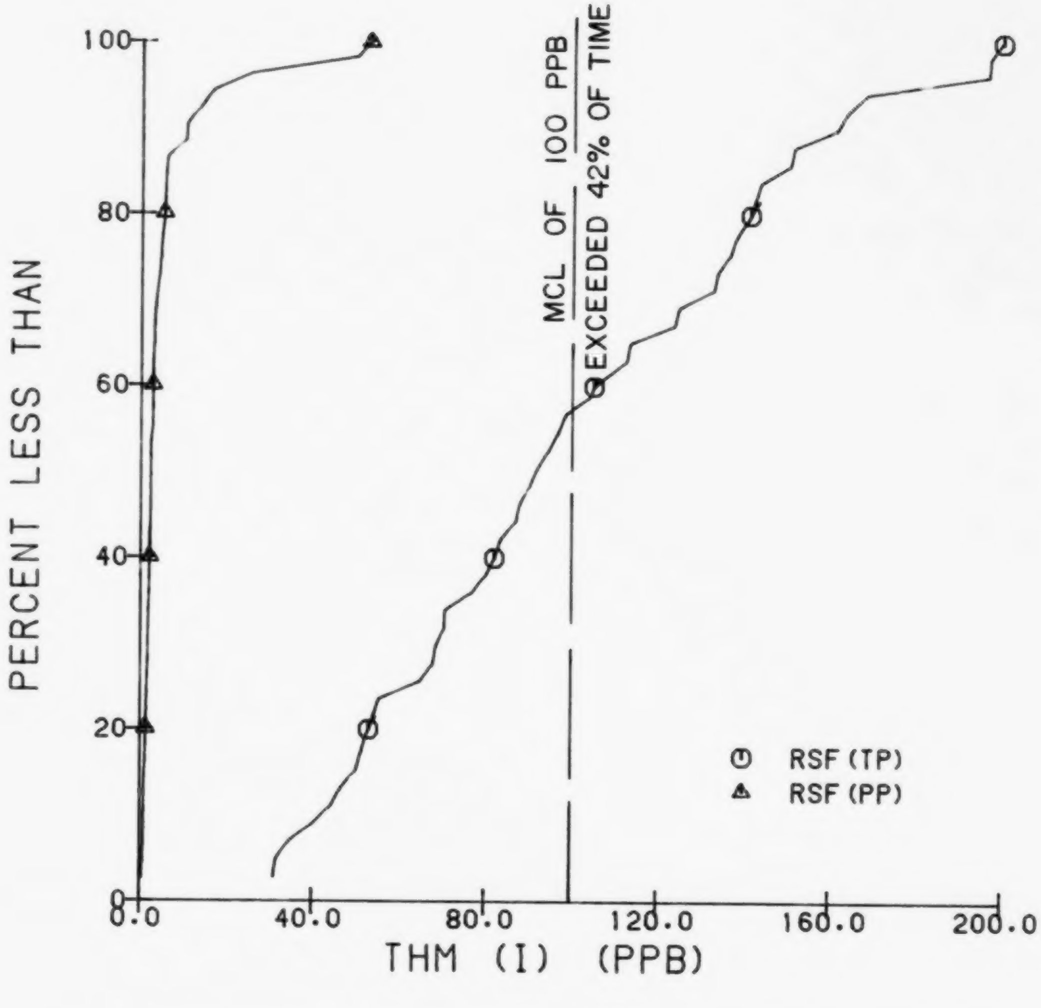


Figure 39. The effect of conventional treatment on THM(I) levels (4/80 to 4/81).

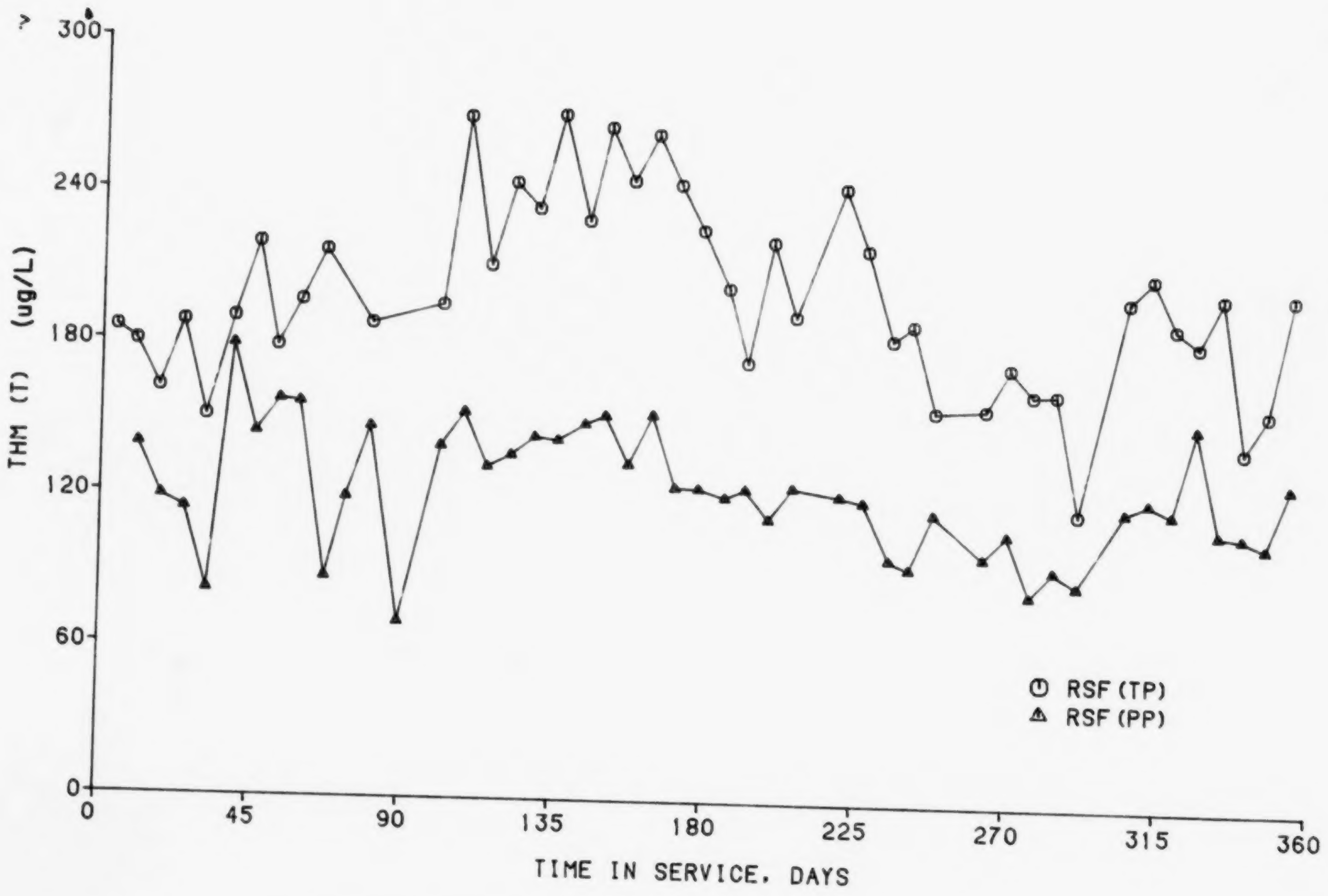


Figure 40. Terminal THM levels in the rapid sand filter effluents.

Torresdale for disinfection (165). On the other hand, acetone is somewhat biodegradable and may have been found in higher concentrations through the Torresdale Plant due to bacterial oxidation of the acetone through the undisinfected Pilot Plant conventional treatment processes. Figure 41 shows 1,2-dichloropropane (DCP) levels in the Torresdale and Pilot Plant rapid sand filter effluents. DCP was consistently found in concentrations of greater than 1 ppb. Note that although the DCP concentrations in both effluents were 'in phase', DCP concentrations were consistently higher through the Torresdale Plant.This difference, which is further addressed in the Discussion Section of this report, may be due to the different raw water intake cycles of the two plants.

GC profiles were used to present broad spectrum analysis of semi-volatile organic compounds collected by XAD-2/8 resin accumulators for the period of May 2 to August 1, 1980. The XAD-2/8 accumulator collects non-polar organics of boiling points ≈ C6 (hexane) to C26 (hydrocarbons). Table 43 shows the GC/MS analysis of the May 17, 1980 rapid sand filter samples from the Torresdale and Pilot Plants and the effluent of the ozonation process at the Torresdale Plant. Kovat's Indices (KI) are assigned for all compounds above 800 KI by GC/MS scan numbers and comparison with the GC profiles. Table 43 also shows the GC/MS tentative identification of 23 compounds below a KI of 800. These 23 compounds are not observed by GC profile analysis because of the solvent effect and on-column injection utilized for GC capillary analysis.

The compounds isolated by the resin method (Table 43) confirm the identity of those isolated by purge and trap analysis (Table 42). The compounds confirmed by the resin method are the four haloforms, DCP, trichloroethylene, tetrachloroethylene, the C-2 benzene isomers (ethyl benzene and ortho- and meta-xylene), the C-3 benzene isomers (e.g. cumene), the dichlorobenzene isomers (e.g. o-dichlorobenzene). Also, within the retention time range of the purge and trap method (up to KI = 1000), a series of chloromethyl butene and butane isomers, 2 tetrahydrofuran isomers, 3 hexanones, 2 hexanols, 4 C-7 and 8 branch hydrocarbons, benzonitrile, benzaldehyde, cyclohexene, 1, 1-diethoxyethane and 1,1,1-trichloroactone were observed. These are probably some of the unknown peaks observed in the purge and trap GC analysis.

Table 44 shows the average peak distribution (between selected Kovats Indices) for the Pilot Plant and Torresdale Plant rapid sand filter effluents during 10 sampling periods. The average number of peaks isolated from the Torresdale Plant was 233. This compares with 167 from the Pilot Plant. These numbers include peaks caused by the blanks. The Quality Assurance Data (Appendix B) indicate that when 150 L were composited for each sample, only a 10% efficiency of recovery occurred. The detection limit for the GC profiles from the MRR analysis is three orders of magnitude more sensitive than the purge and trap analysis, with a detectable limit of 0.2 ng/L (ppt).

Table 44 also shows that 25% of the average GC peak distributions at the Torresdale RSF have concentrations above 2 ng/L. This corresponds well with Table 43 which indicates that 33% of the 233 GC peaks in the RSF effluent of 5/17/80 were identified. Similarly, 16% of the average GC peak distributions at the Pilot Plant RSF have concentrations above 2 ng/L. This compares with 13% of the 167 GC peaks in the RSF effluent for 5/17/80 being identified.

TABLE 43. GC/MS TENTATIVE IDENTIFICATIONS AND THEIR RESPECTIVE AVERAGE KOVATS INDICES ON A SE-30 CAPILLARY COLUMN FOR PILOT PLANT AND TORRESDALE OZONATOR INFLUENTS AND TORRESDALE OZONATOR EFFLUENT (SAMPLING PERIOD ENDING DATE = 5/17/80)

Peak No. (T)		Compounds Tentatively Identified	Kovats Index[a]	RSF Effluent (PP)	RSF Effluent (TP)	O_3 RT (TP)
<C7		C7 branched HC			X	
		Cyclohexane		X	X	X
		C7 branched HC		X	X	
		C7 branched HC			X	
	P	1,2-Dichloropropane		X	X	X
		Chloromethyl butene is			X	
	P	Dichlorobromomethane		X	X	X
	P	Trichloroethylene		X	X	X
		Cis or trans-2,5-dimethyl tetrahydrofuran		X	X	X
		Methyl methacrylate-B		X	X	X
		Cis or trans-2,5-dimethyl tetrahydrofuran		X		X
		Chloromethyl butene is			X	
		Hexanone isomer			X	
		1,1-Diethoxyethane			X	
		Chloromethyl butene is			X	
		1,1,1-trichloroacetone			X	
		Chloromethyl butene is			X	
	P	Toluene		X	X	
		3-Hexanone			X	
		2-Hexanone		X	X	
	P	Dibromochloromethane		X	X	X
		C8 branched HC			X	
		3-Hoxanol			X	
		Hoxanol isomer			X	
0.	P	Tetrachloroethylene	797.9	X	X	X
		C-8	800			
1.		2,3-dichloro-2-methyl butane	804.9		X	
2.		C2-benzene and	847.9		X	
3.	P	bromoform	852.3		X	

Table 43 (Continued)

Peak No.(T)	Compounds Tentatively Identified	Kovats Index^{a}	RSF Effluent (PP)	RSF Effluent (TP)	O_3 RT (TP)
4.	P^{c} C2-benzene	854.7		X	
*		859.2			
*		867.5			
*		869.5			
5.	styrene-B	871.7		X	
6.	C2-benzene	876.4	X	X	
7.	C2-benzene	884.6^{b}			
	C-9	900			
8.	C3-benzene	908.8	X	X	
*		916.9			
9.	benzaldehyde	925.6	X	X	X
*		930.1			
10.	benzonitrile	943.9		X	
11.	C3-benzene	946.3		X	
*		950.3			
*		950.8			
12.	C3-benzene	963.3		X	
13.	C3-benzene	978.2		X	
*		980.2			
*		983.5			
14.	P dichlorobenzene	987.1		X	
	C-10	1000			
15.	P dichlorobenzene	1008.5		X	
16.	2-ethyl-1-hexanol	1014.6		X	
17.	acetophenone	1031.6	X	X	X
*		1058.3			
18.	methyl benzoate-B	1068.3	X	X	X
19.	tolunitrile +	1088.4	X	X	X
19A.	P isophorone	1088.4	X	X	
	C-11	1100			
*		1103.6			
20.	camphor	1118.0^{b}			
21.	C2-benzaldehyde	1131.3	X	X	X
22.	C2-benzaldehyde	1146.9	X	X	
23.	P trichlorobenzene	1152.8	X	X	

Table 43 (Continued)

Peak No.(T)	Compounds Tentatively Identified	Kovats Index^a	RSF Effluent (PP)	RSF Effluent (TP)	O_3 RT (TP)
24.	2-isopropyl-5-methyl-1-cylclohexanol or isomenthol or menthol	1156.9		X	
25.	P naphthalene-B	1158.8	X	X	
*		1185.0			
*		1187.8			
26.	benzothiazole	1189.4^b			
	C-12	1200			
27.	1-nitrooctanone-B	1221		X	
28.	nitrooctanone-B	1227		X	
29.	C-2 acetophenone	1231.9	X	X	X
30.	1,2-bis(2-chloroethoxy) ethane	1237.2	X	X	
31.	C-2 acetophenone	1250.4	X	X	
32.	t-butylphenol	1268.8			
33.	C2-methyl benzoate-B	1269.2		X	
*		1270.8			
34.	Diacetone-sugar	1274.8		X	
	C-13	1300			
35.	Diacetone-sugar	1376.4	X		
36.	Diacetone-D-xylose	1396.4	X	X	
	C-14	1400			
37.	P dimethylphthalate	1409.5		X	
38.	dihydroactinidiolide	1487.1		X	
	C-15	1500			
39.	FAME	1506.6	X	X	
40.	diethyl phthalate	1551.1	X	X	
41.	Diacetone-L-sorbose	1573.6	X	X	X
42.	Diacetone-sugar^b	1583.4			
	C-16	1600			
43.	Diacetone-sugar	1619.0		X	
44.	FAME	1643.1		X	
45.	Simazine	1686.0		X	
	C-17	1700			

Table 43 (Continued)

Peak No.(T)	Compounds Tentatively Identified	Kovats Index[a]	RSF Effluent		O_3 RT
			(PP)	(TP)	(TP)
45.5	FAME	1707.3		X	
*		1718.5			
		1724.5			
46.	FAME	1744.0	X	X	X
47.	FAME	1722.7		X	
*		1777.3			
	C-18	1800			
	C-19	1900			
47.5	FAME	1908		X	
48.	P dibutyl phthalate	1918.2		X	
	C-20	2000			
	C-21	2100			
	C-22	2200			
	C-23	2300			
	C-25	2500			
	C-26	2600			
49.	FAME	2820	X		

*Where there are no numbers a mass spectra was obtained but no identification has been made.

T - All tentative identifications. No retention time data was obtained.

P - Priority Pollutants

FAME - Fatty Acid Methyl Ester

B - Blank - See Appendix B, Quality Assurance

[a] Kovat Index - based upon GC/MS Scan Number

[b] Where there are no X's present, these compounds were identified in other samples

[c] only ethyl benzene is on the Priority Pollutant list

TABLE 44. AVERAGE PEAK DISTRIBUTION FOR PILOT PLANT AND TORRESDALE RAPID SAND FILTER EFFLUENTS FOR SAMPLING PERIODS 5/2 TO 8/1/80 (10 SAMPLING PERIODS)[a,b]

Torresdale Plant

Concentration (ng/l)	Kovats Index 800 to 1100	1100 to 1400	1400 to 1700	1700 to 2000	2000 to 2600	Total
0.2 to 0.7	19	14	11	10	12	96
0.7 to 2.0	24	17	14	12	15	82
2.0 to >20	16	12	9	8	10	55
Total	59	43	34	30	37	233

Pilot Plant

Concentration (ng/l)	Kovats Index 800 to 1100	1100 to 1400	1400 to 1700	1700 to 2000	2000 to 2600	Total
0.2 to 0.7	12	13	16	15	17	73
0.7 to 2.0	11	12	15	14	15	67
2.0 to >20	5	5	6	6	7	27
Total	28	30	37	35	39	167

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[a] Assuming only 10% recovery, and all responses are equivalent to the internal standard, a C-23 hydrocarbon. (see Quality Assurance (MRR) for a discussion of percent recovery.) - Appendix B

[b] The data includes compound identified in blanks. (See Quality Assurance (MRR) Section.) - Appendix B

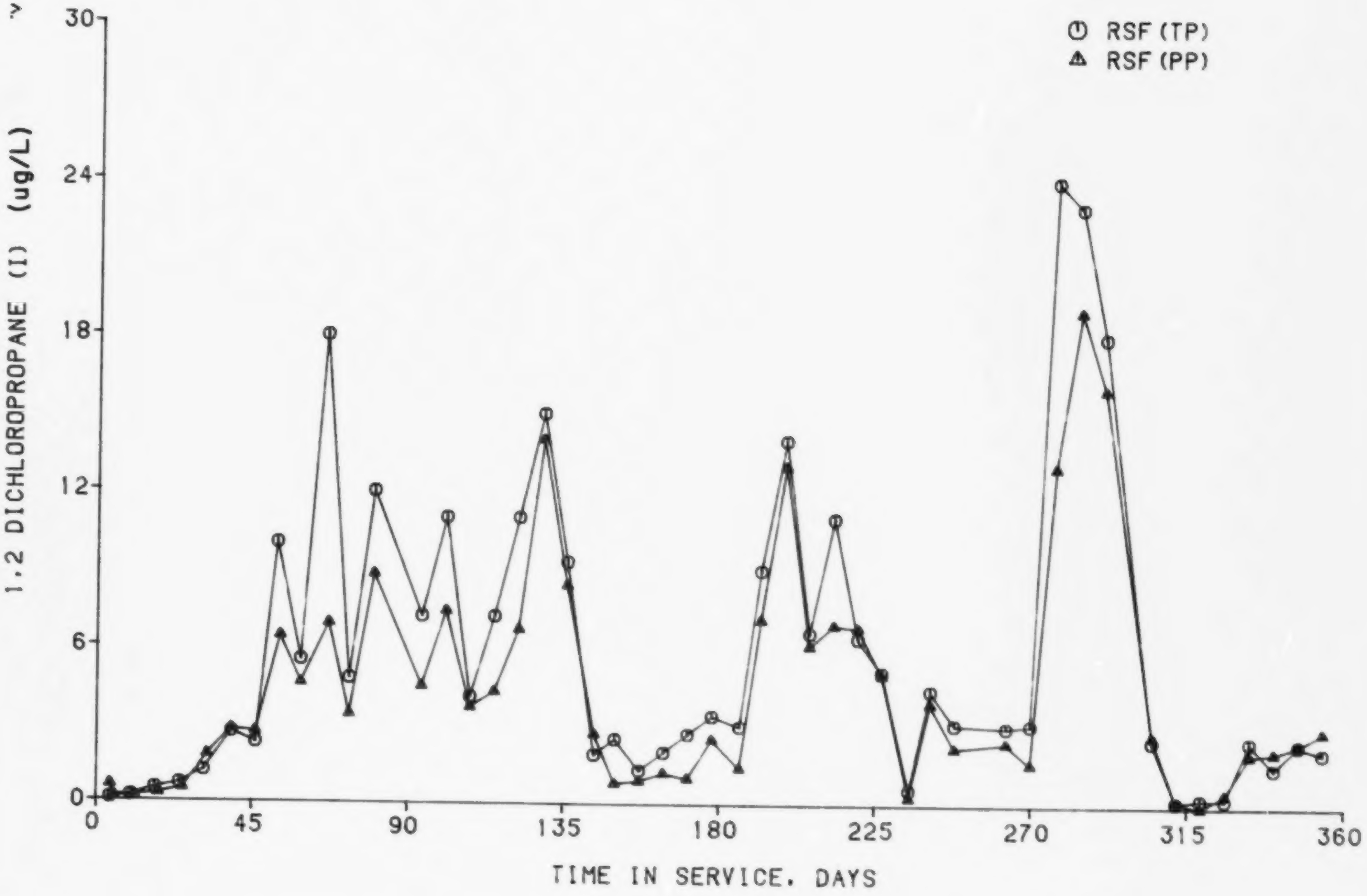

Figure 41. 1,2-Dichloropropane levels in the rapid sand filter effluents.

This indicates that most of the more concentrated organics (>2 ng/L) present in the samples collected by the XAD resin sampler were identified by GC/MS. Most of the complement of organics observed in Table 43 have been previously identified in Torresdale drinking water (166).

Advanced Water Treatment Systems

The above results demonstrated the very different organic qualities of the Torresdale and Pilot Plant conventional treatment system effluents. The following discussion shows the efficacy of various advanced water treatment (AWT) systems and how they were affected by the organic characteristics of the applied waters. The advanced water treatment systems are defined here to include the unit processes of ozonation and GAC adsorption, as well as the combined unit processes of ozone/GAC and ozone/sand. The results for each process are separated between the general organic parameters of DOC, THMFP and A254 absorbance and the specific organics, as measured by the purge and trap analysis and XAD resin accumulators.

Ozonation System --

The ozonation system had two major effects on the organics in its incoming water: oxidation (by ozone or oxygen) and volatilization. Oxidation was most apparent when examining the general organic parameters of DOC, A254 and THMFP. Volatilization, on the other hand, mainly effected only the lighter molecular weight organic compounds (such as DCP and chloroform).

General Organic Parameters -- Ozonation had a consistent effect on the organics through both the Torresdale and the Pilot Plant ozone contactors. A summary of the average DOC, A254 and THMFP concentrations through the two ozonation systems is presented in Table 45. The effect of ozonation on DOC is also shown in Figure 42. Note that although the Torresdale ozonation system was applied with a higher DOC loading rate than the Pilot Plant ozonation system, it was not as effective as the Pilot Plant system in reducing the DOC concentration in the water.

Figure 43 shows the change in A254 through the two ozonation systems. Unlike DOC, UV absorbance levels in the rapid sand filter effluents of the two plants were nearly identical. Like the DOC results, however, ozonation of the Pilot Plant water resulted in greater decreases in A254 than were observed for the Torresdale Plant Water. In fact, the decrease in absorbance for the nonchlorinated, Pilot Plant water was nearly twice that found for the chlorinated, Torresdale Plant water.

Figures 44 and 45 show THMFP removals through the Torresdale and Pilot Plant ozone contactors, respectively. Here the difference between the chlorinated and non-chlorinated systems is most evident: while the Pilot Plant system consistently lowered the THMFP levels, the Torresdale system showed a consistent THMFP increase. THMFP levels dropped an average of 16% in the Pilot Plant but increased an average of 6% in the Torresdale Plant ozonation

TABLE 45. OZONE CONTACTOR PERFORMANCE COMPARISON[1] (4/80 - 4/81)

Site	DOC			A254			THMFP		
Torresdale	ppb	Δ(ppb)	%Δ	A254	Δ(A254)	%Δ	ppb	Δ(ppb)	%Δ
(5) RSF	2559	--	--	0.137	--	--	99	--	--
(6C) O_3C	2451	108	4%	NA[2]	--	--	NA	--	--
(6D) O_3RT	2452	107	4%	0.102	0.035	26%	105	-6	-6%
Pilot Plant									
(14) RSF	1826	--	--	0.135	--	--	119	--	--
(15C) O_3C	1662	164	9%	NA	--	--	NA	--	--
(15D) O_3RT	1622	204	11%	0.069	0.066	49%	100	19	16%
(19) $O_3/SAND_{15}$	1395	431	24%	NA	--	--	86	33	28%

Δ(ppb) and %Δ based on RSF Values

[1] Weighted averages of 30-minute composites collected once per week for 52 weeks.

[2] NA = Not Available.

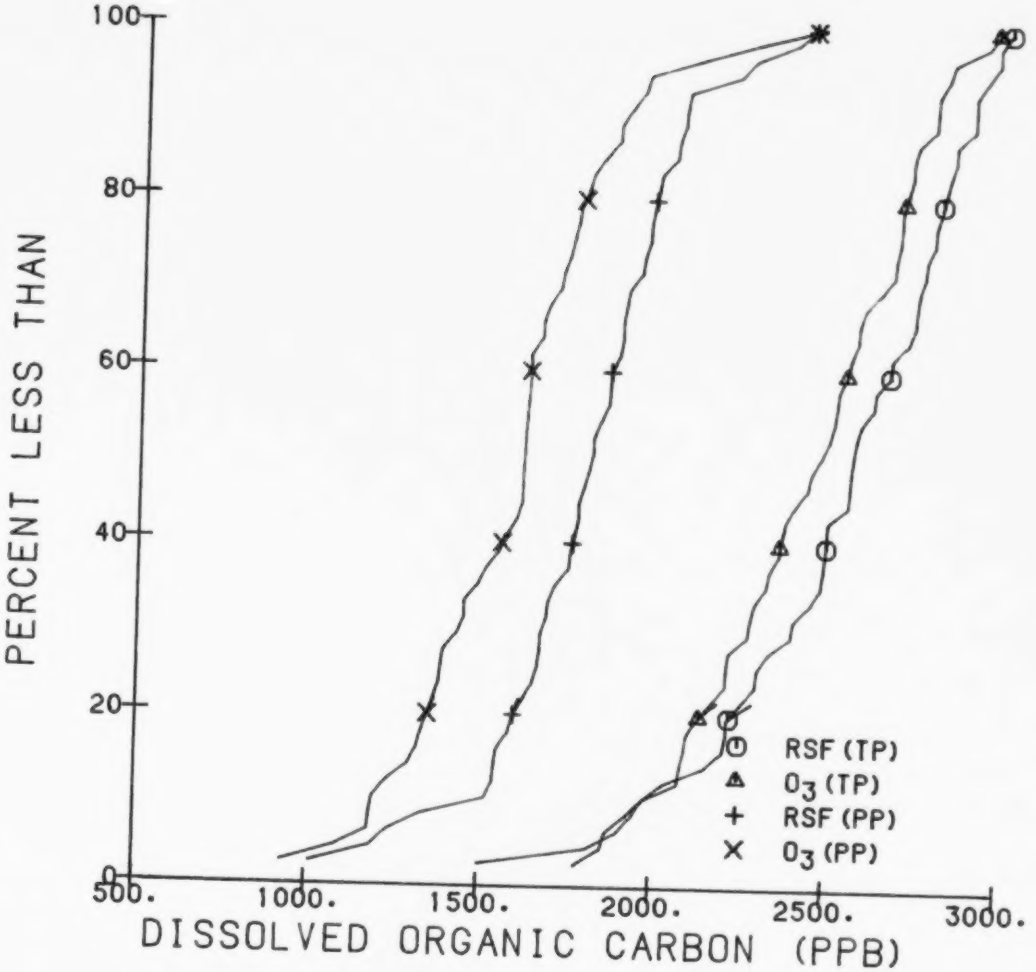

Figure 42. The effect of ozonation on DOC levels (4/80 to 4/81).

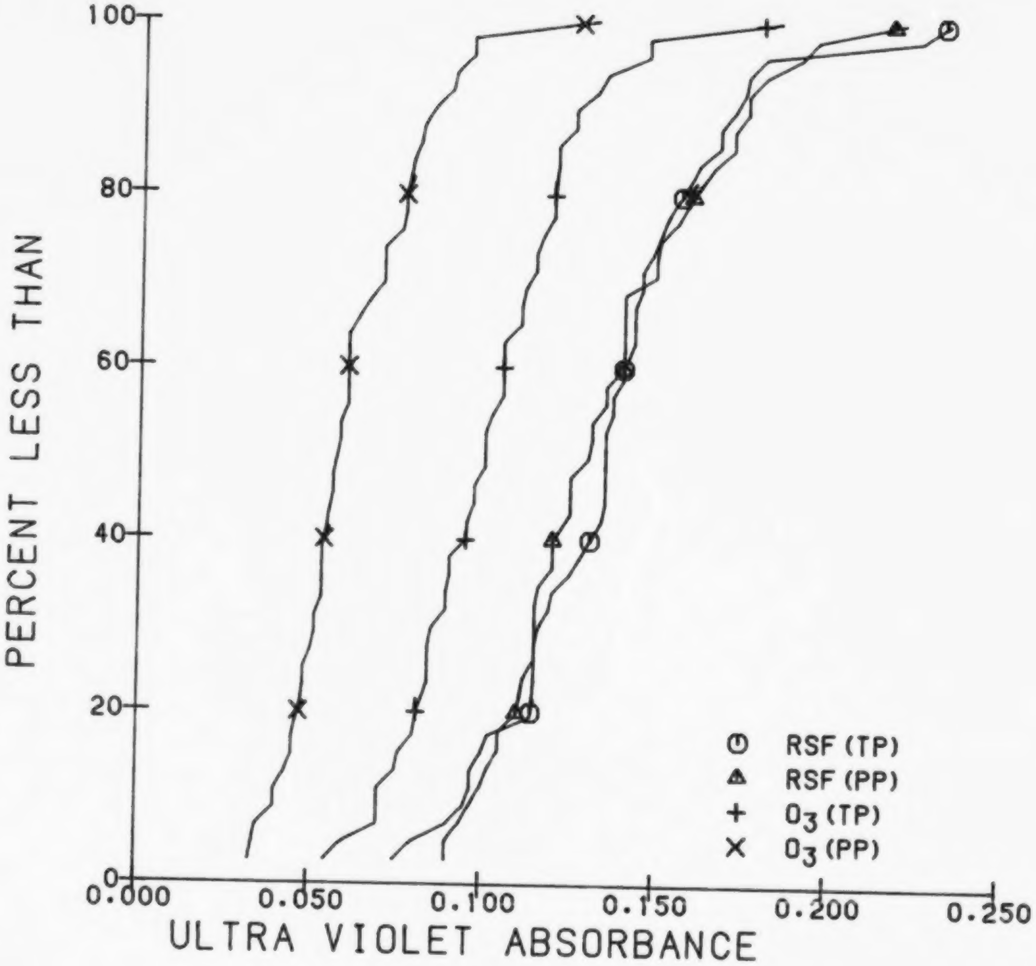

Figure 43. The effect of ozonation on A254 absorbance (4/80 to 4/81).

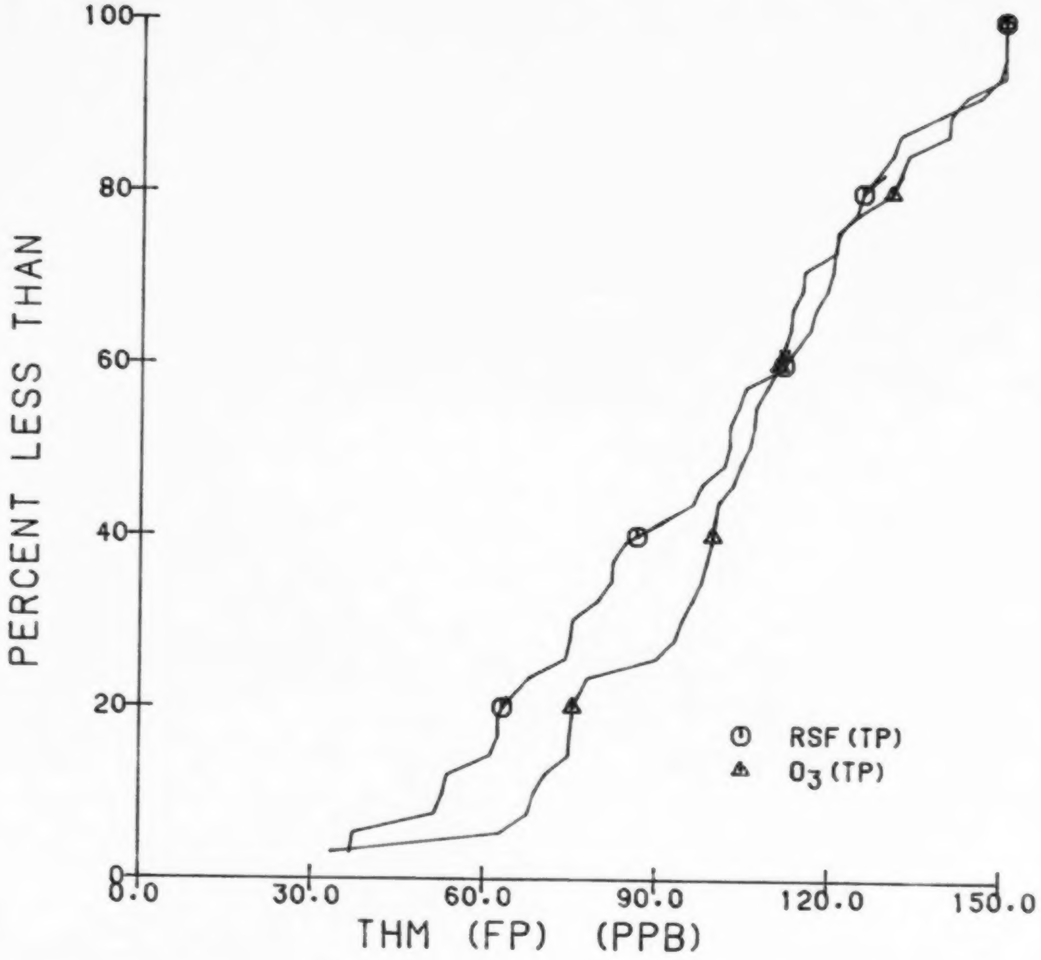

Figure 44. The effect of ozonation on THMFP in the Torresdale Plant (4/80 to 4/81).

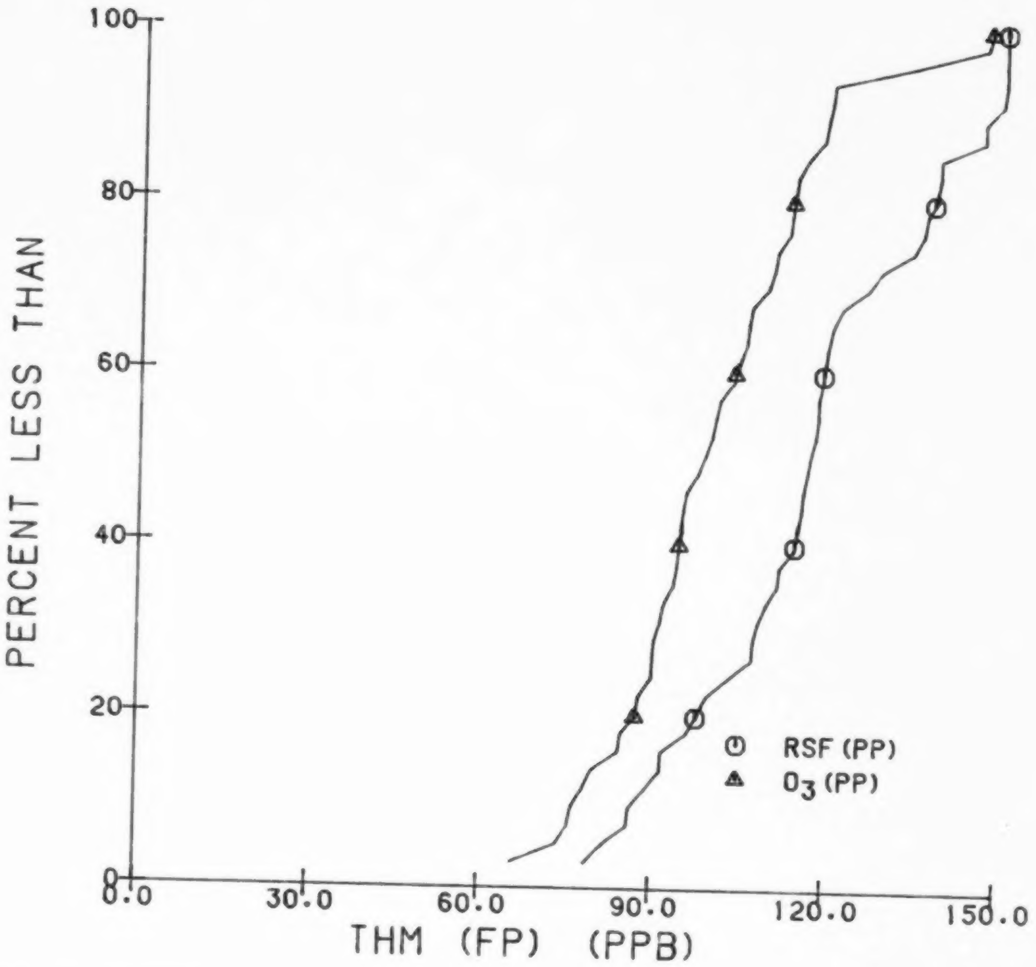

Figure 45. The effect of ozonation on THMFP in the Pilot Plant (4/80 to 4/81).

system (see Table 45). This is consistent with laboratory ozonation work. This indicates that most of the more concentrated organics (>2 ng/L) present in the samples collected by the XAD resin sampler were identified by GC/MS. Most of the complement of organic observed in Table 43 have been previously identified in Torresdale drinking water (166).

As another measure of the oxidative ability of the ozone process, DOC levels were also determined through a 15 minute EBCT sand bed which received ozonated Pilot Plant water. This sand bed, although incapable of any significant levels of organic adsorption, was capable of retaining high levels of bacteria. As will be shown in the discussion of the minicolumn results, these bacteria metabolize organics in the process stream which are readily biodegradable. This sand system provided a means to observe the relative biodegradability of the organics in the ozone contactor effluent. Figure 46 shows the DOC levels in and out of the contactor and the $O_3/SAND_{15}$ system. While DOC reductions averaged 204 ppb through the ozonation system, an additional 227 ppb DOC was removed through the sand bed. To confirm that all of the DOC which was readily biodegradable in the process stream was removed, the effluent from the $O_3/SAND_{15}$ system was applied to another sand bed, also of 15 minute EBCT. The effluent DOC levels from the second sand column ($O_3/SAND_{30}$) did not differ significantly (t-test with $a = 0.05$) from those of the $O_3/SAND_{15}$ system, indicating that 15 minutes was a sufficient contact time for the removal of all readily biodegradable organics.

Another 15 minute EBCT sand bed was established following the Pilot Plant rapid sand filters ($SAND_{15}$). Its purpose was to determine whether biodegradable organics remained in the process stream following rapid sand filtration. The results showed no statistically significant DOC removal capabilities (t-test with $a = 0.05$), indicating that the DOC removal through the $O_3/SAND_{15}$ system was a result of organic oxidation in the ozone contactor. Because there were no biodegradable organics in the influent or the effluent from the $O_3/SAND$ system, it was considered a useful tool in determining the effectiveness of the ozonation process for making organics more biodegradable. However, similar tests could not be performed through the Torresdale system since the chlorine residual would inhibit any significant bacterial activity.

Figure 47 presents THMFP results through the Pilot Plant ozone contactor and associated sand beds. Similar to the DOC results, THMFP was removed in the sand beds as well as in the ozone contactor. Again, for the Torresdale Plant, no THMFP would be removed through a sand bed since a residual disinfectant is present.

Specific Organics--Since aeration is a significantly less expensive process than ozonation, knowledge of whether stripping or oxidation is the dominant mechanism for specific organic removal becomes critical for the optimum design of an ozonation system. Laboratory scale aeration of Delaware River water showed between 12% and 28% of the organic carbon present could be stripped (see Table 39). Many of the more hazardous organic substances found in the water supply are low molecular weight organic compounds which remain stable upon ozonation. Typically, these compounds have Henry's law coefficients greater than 1×10^{-3} atm-m^3/mole and are therefore easily removed through stripping (167).

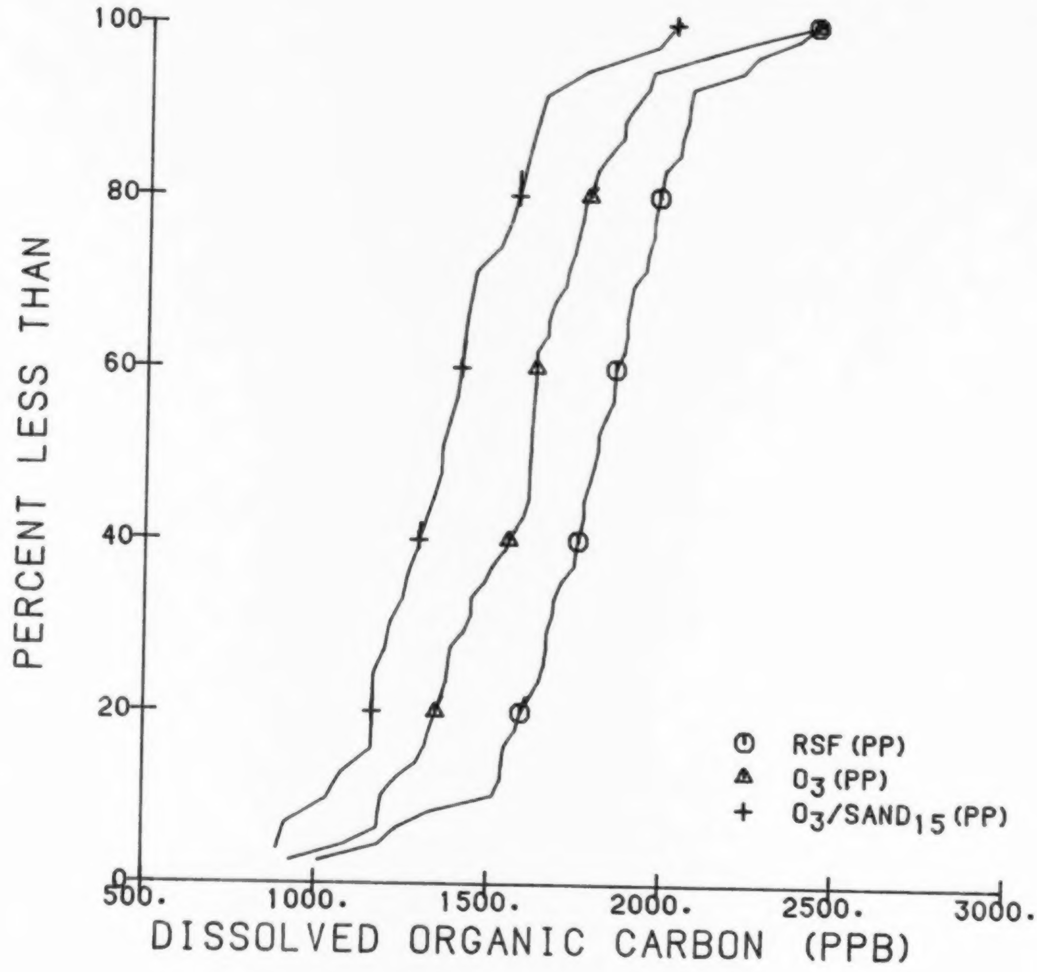

Figure 46. DOC levels through the Pilot Plant ozone and ozone/sand systems (4/80 to 4/81).

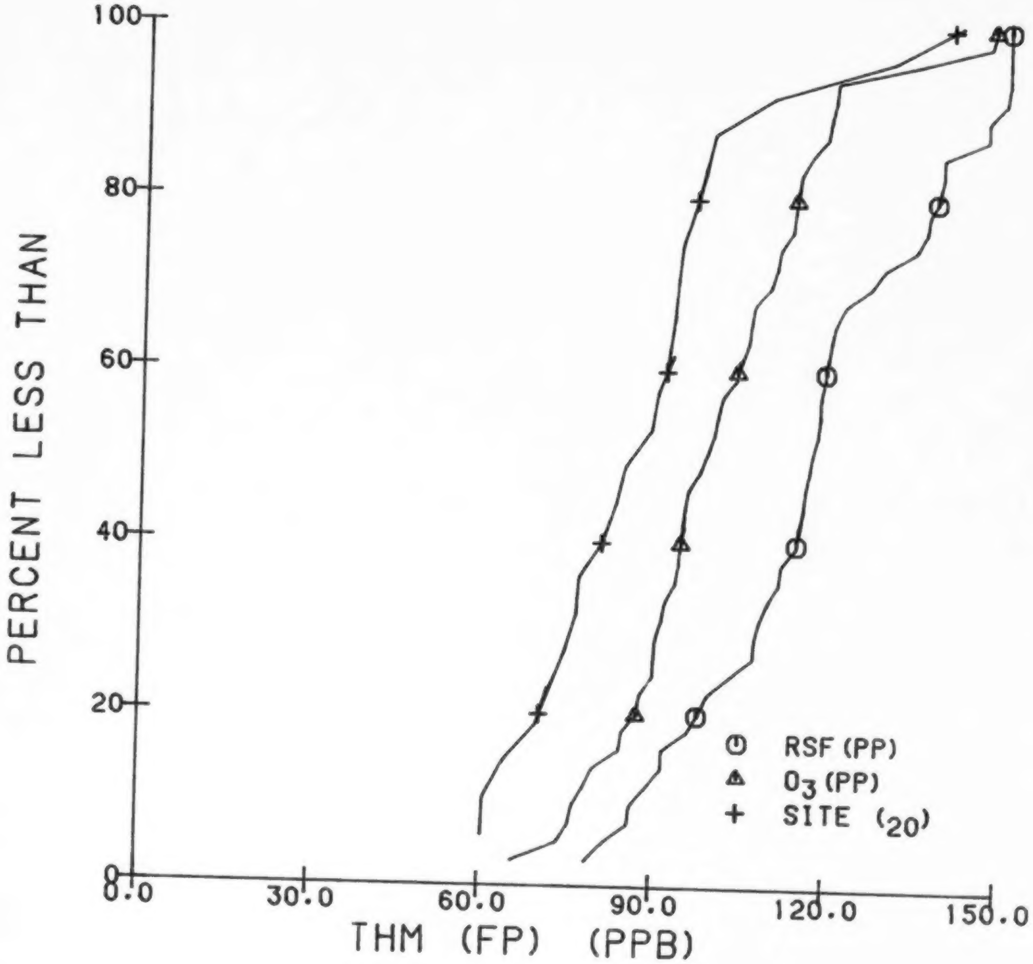

Figure 47. THMFP levels through the Pilot Plant ozone and ozone/sand systems (4/80 to 4/81).

A good example of this class of compounds is chloroform (167). Figure 48 shows the effect of stripping on chloroform in the Torresdale ozone contactor. Figures 49 to 51 show the cumulative distribution functions of chloroform, dichlorobromomethane and dibromochloromethane, respectively, through the Torresdale ozone contactor. Bromoform, like all of the trihalomethanes in the Pilot Plant process water, was not graphed due to its typically low concentration. Figures 49 through 51 show that as the concentration of the respective THM increases, the amount removed through stripping increases. The reader is cautioned, however, that the THM concentrations were typically their highest in the summertime, when high water temperatures lead to more efficient stripping.

Two low molecular weight organic compounds showed consistent concentrations above 1 ppb in the rapid sand filter effluent of the two plants: 1,2-dichloropropane and dimethoxymethane. Their influent and effluent concentrations to the ozone contactors of the Torresdale and Pilot Plants are presented in Figures 52 to 55. A slight (but consistent) removal of these compounds may be observed through both ozone contactors.

The only volatile organic compound analyzable by the purge and trap technique and confirmed through GC/MS analysis to have been produced in the ozonation process was acetone. The average influent acetone concentration to the ozone contactor (rapid sand filter effluent, Table 42) was 14 g/L whereas the effluent concentration (Table 46) was 21 g/l. Figures 55 and 56 show the changes in acetone through the Torresdale and Pilot Plant ozonation systems, respectively. Note that in Figure 57 the effluent acetone levels from the O_3/SAND$_{15}$ system are also included. While there appears to have been a net increase in acetone production through the Pilot Plant ozone contactor, acetone was effectively removed in the sand bed.

Quantitative results for some of the specific organic compounds measured in the effluents of the ozonation processes by the purge and trap technique are listed in Table 46. These values may be compared with those observed in the ozonator influents (Table 42). GC/MS confirmations for these compounds are presented in Table 47. Due to their infrequent detection, the data is not plotted. Single compound by compound quantification also cannot determine the effects of unidentified compounds which can increase or decrease during the ozonation process. Therefore, to determine the effect of the ozonation process on purgeable organics, selected GC profiles of purgeables were analyzed to find those peaks whose detector response changed by a factor of two or more in the influent and effluent of the ozonators at the Torresdale and Pilot Plants.

Figure 58 and 59 show examples of spike profiles of purgeables utilizing a flame ionization detector (138,139). These profiles have the ordinate as Relative Detector Response, on a linear scale of zero to two. The response is relative to 1500 counts by the GC computer integrator for the samples. Chloroform is at a relative retention time of 1.00. An increasing peak would indicate formation of by-products of ozonation whereas a decreasing peak indicates aeration or oxidation is occuring.

Table 48 lists the number of peaks which change due to the ozonation

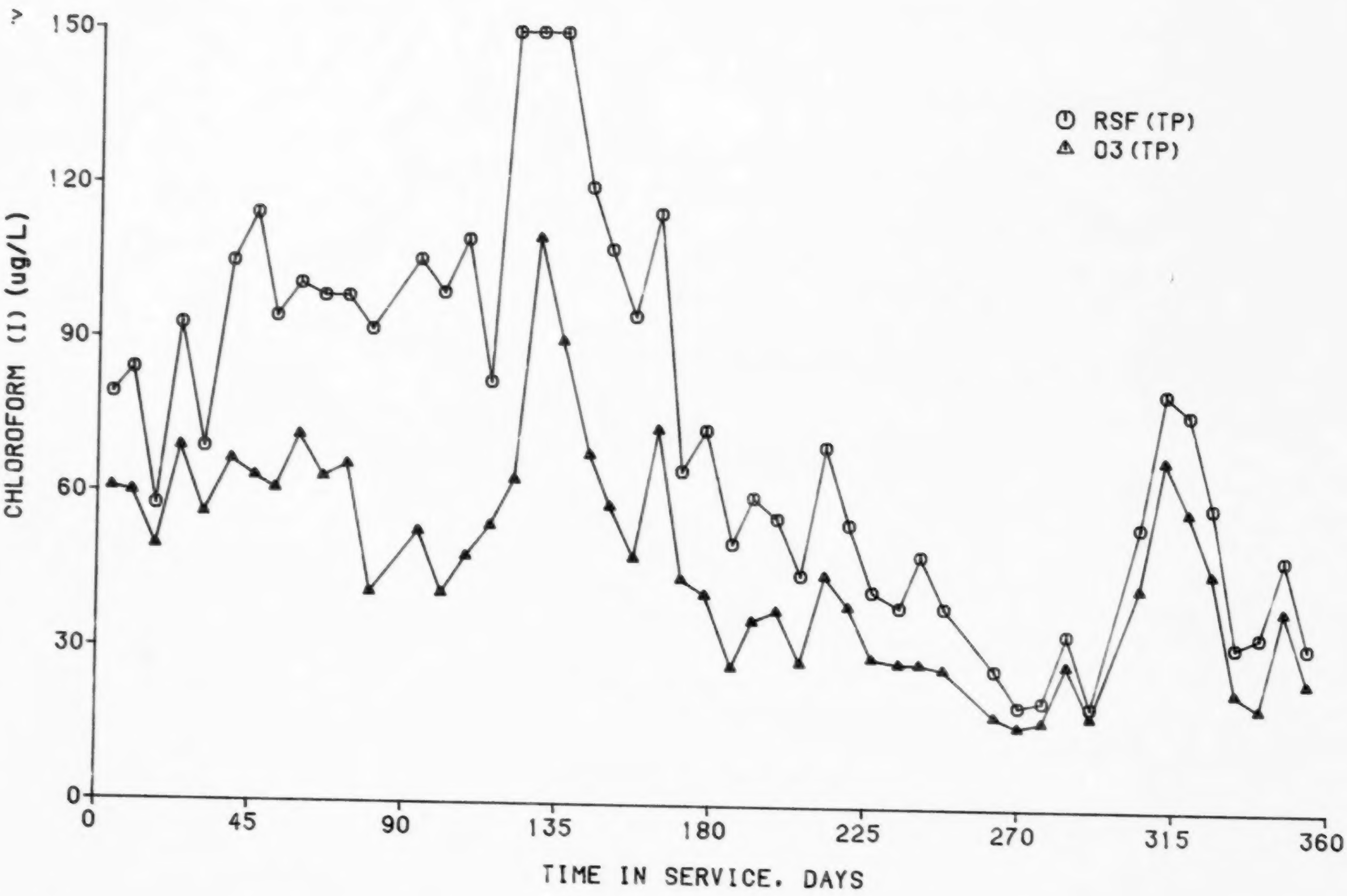

Figure 48. The effect of aeration on chloroform levels through the Torresdale Plant ozone process.

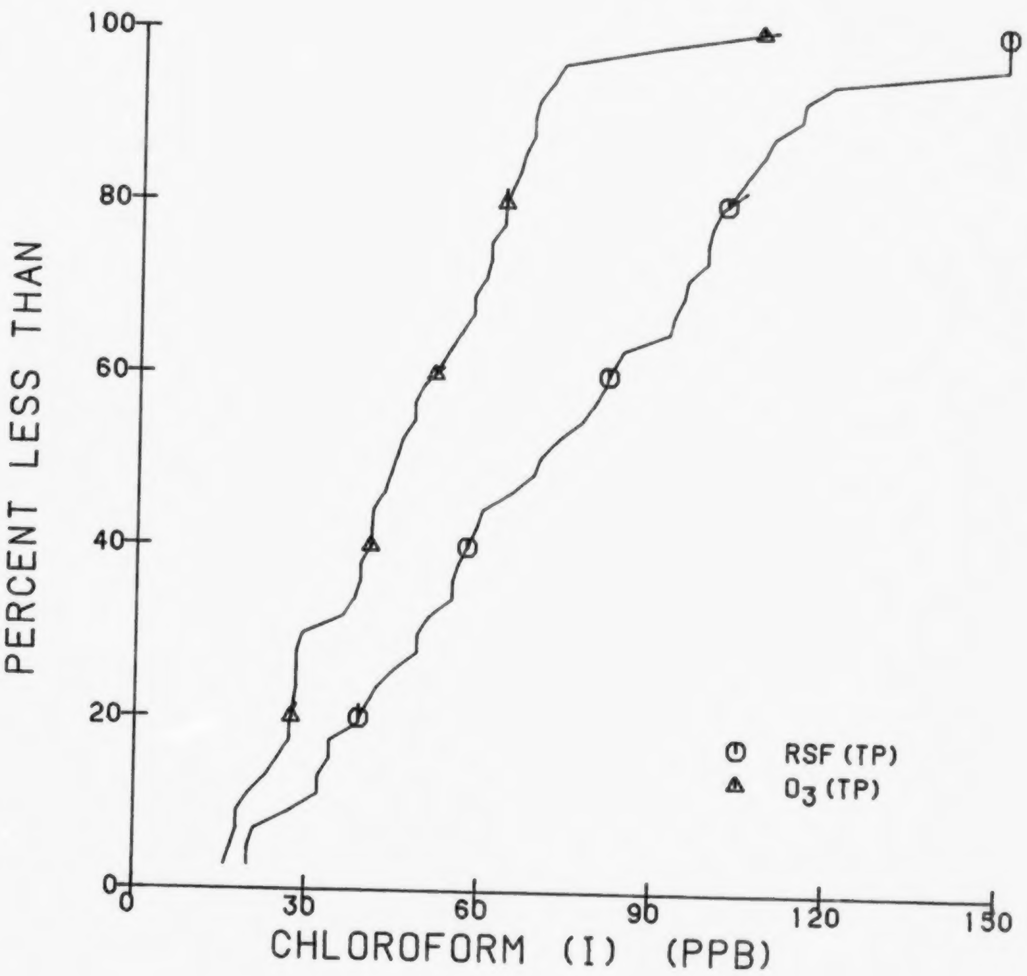

Figure 49. The effect of Torresdale Plant ozonation on chloroform levels (4/80 to 4/81).

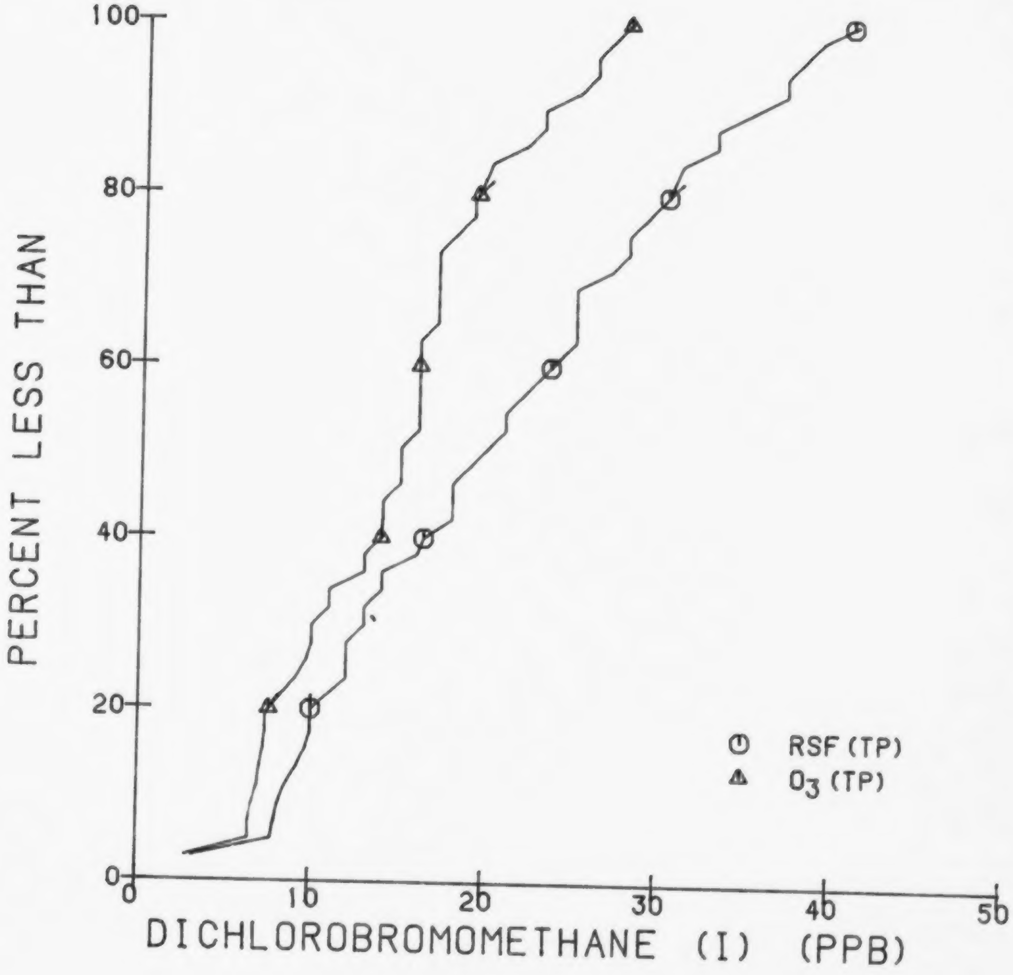

Figure 50. The effect of Torresdale Plant ozonation on dichlorobromomethane levels (4/80 to 4/81).

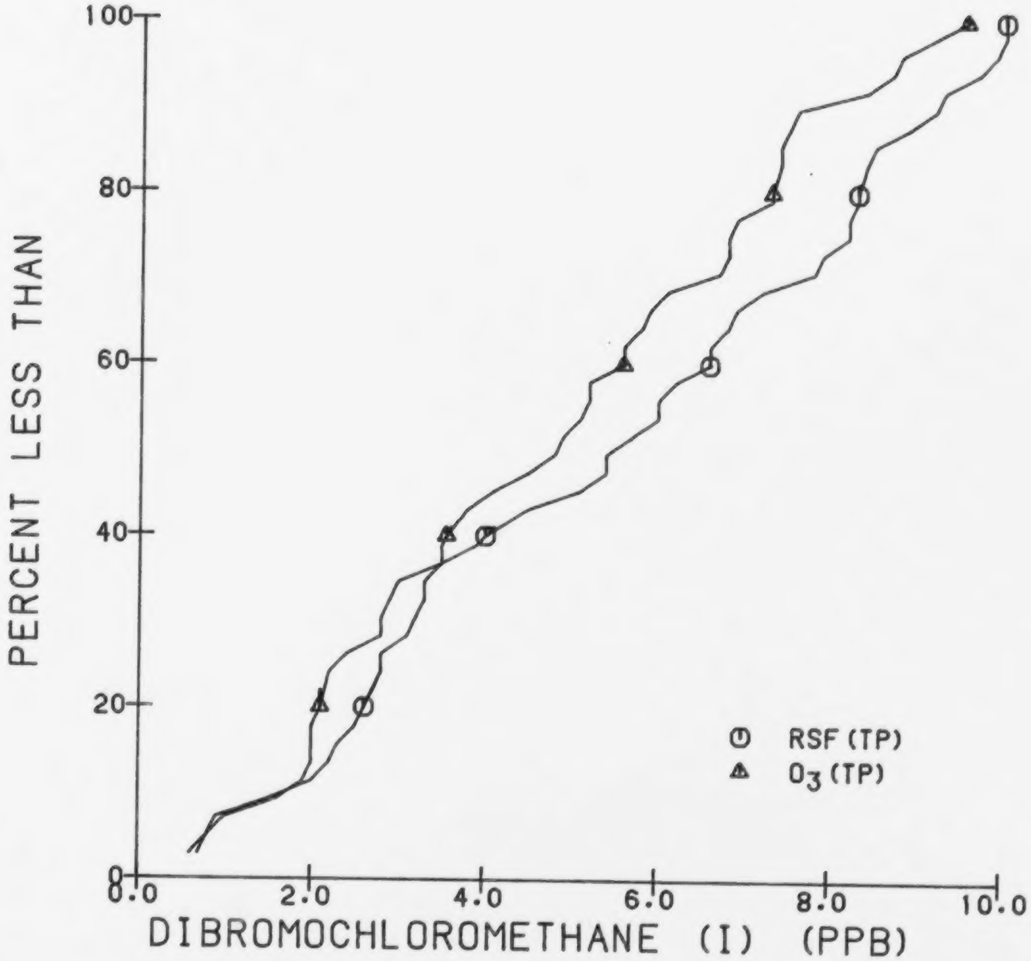

Figure 51. The effect of Torresdale Plant ozonation on dibromochloromethane levels (4/80 to 4/81).

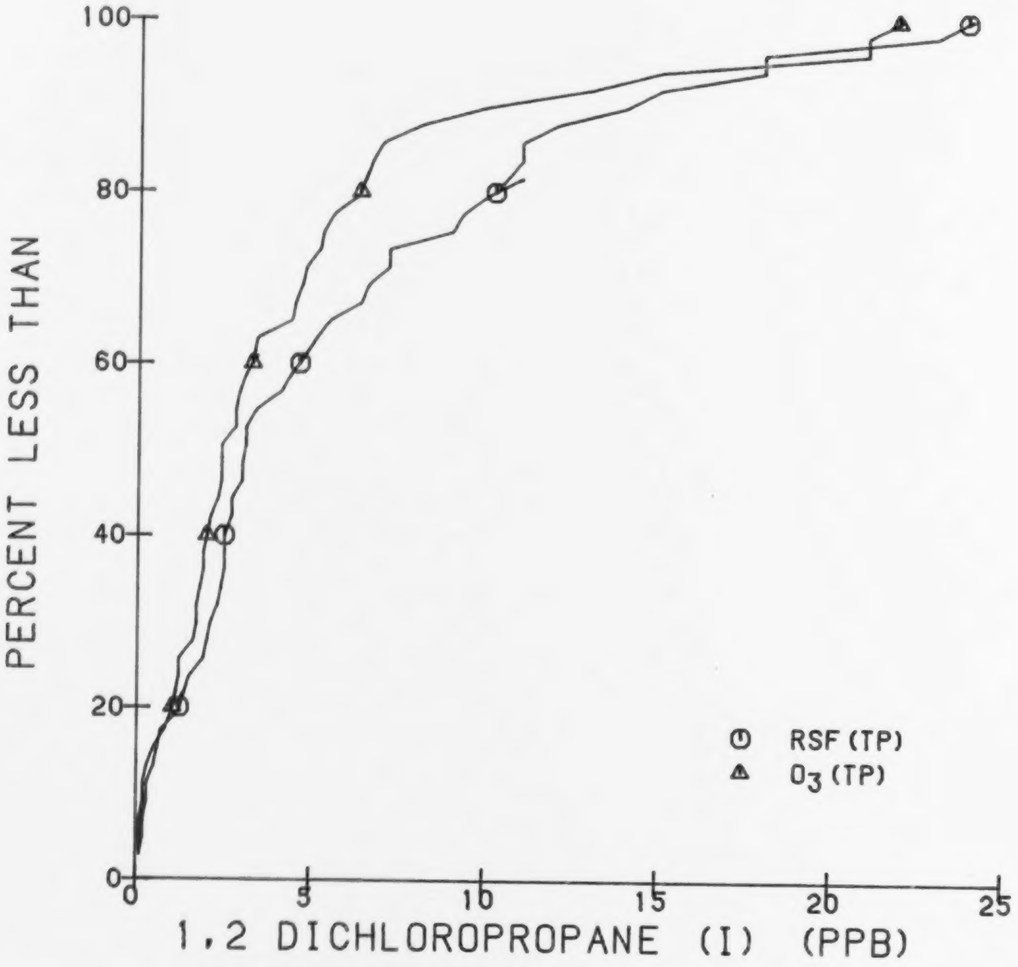

Figure 52. The effect of Torresdale Plant ozonation on 1,2-dichloropropane levels (4/80 to 4/81).

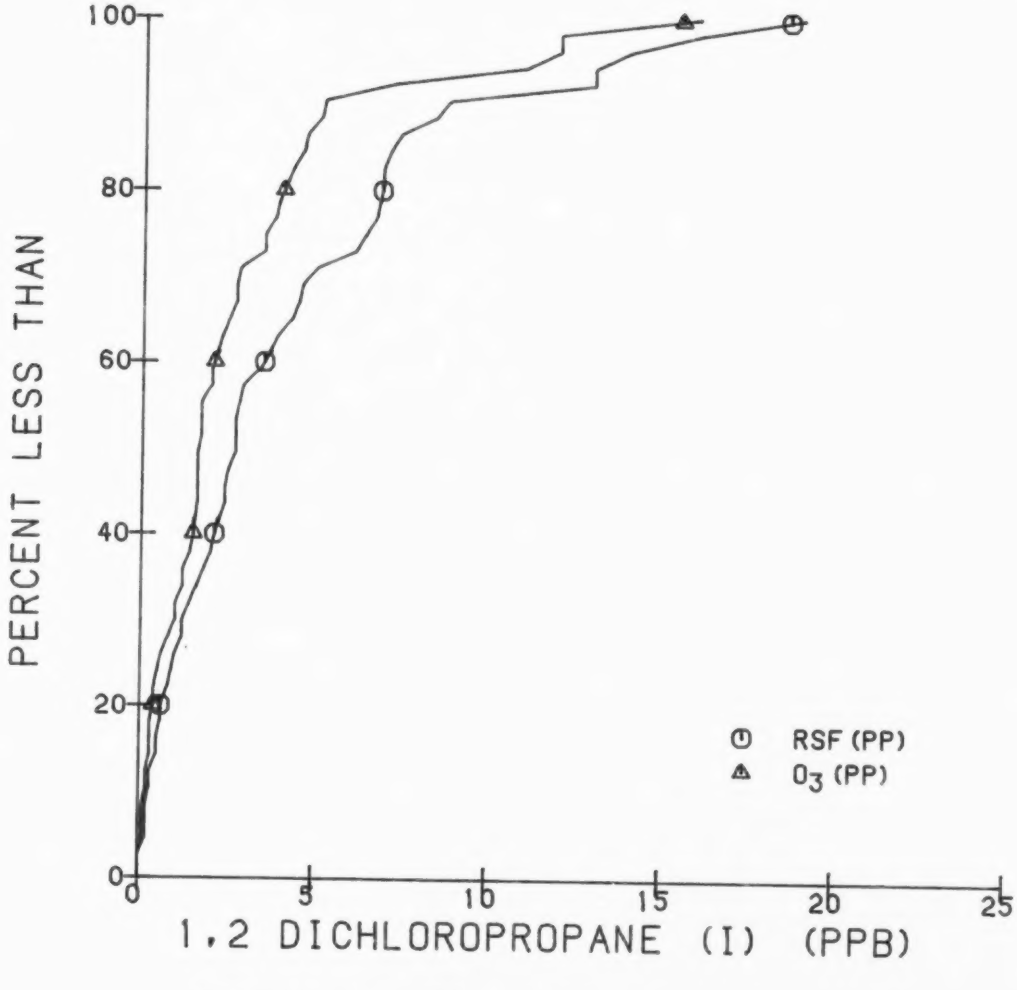

Figure 53. The effect of Pilot Plant ozonation on 1,2-dichloropropane levels (4/80 to 4/81).

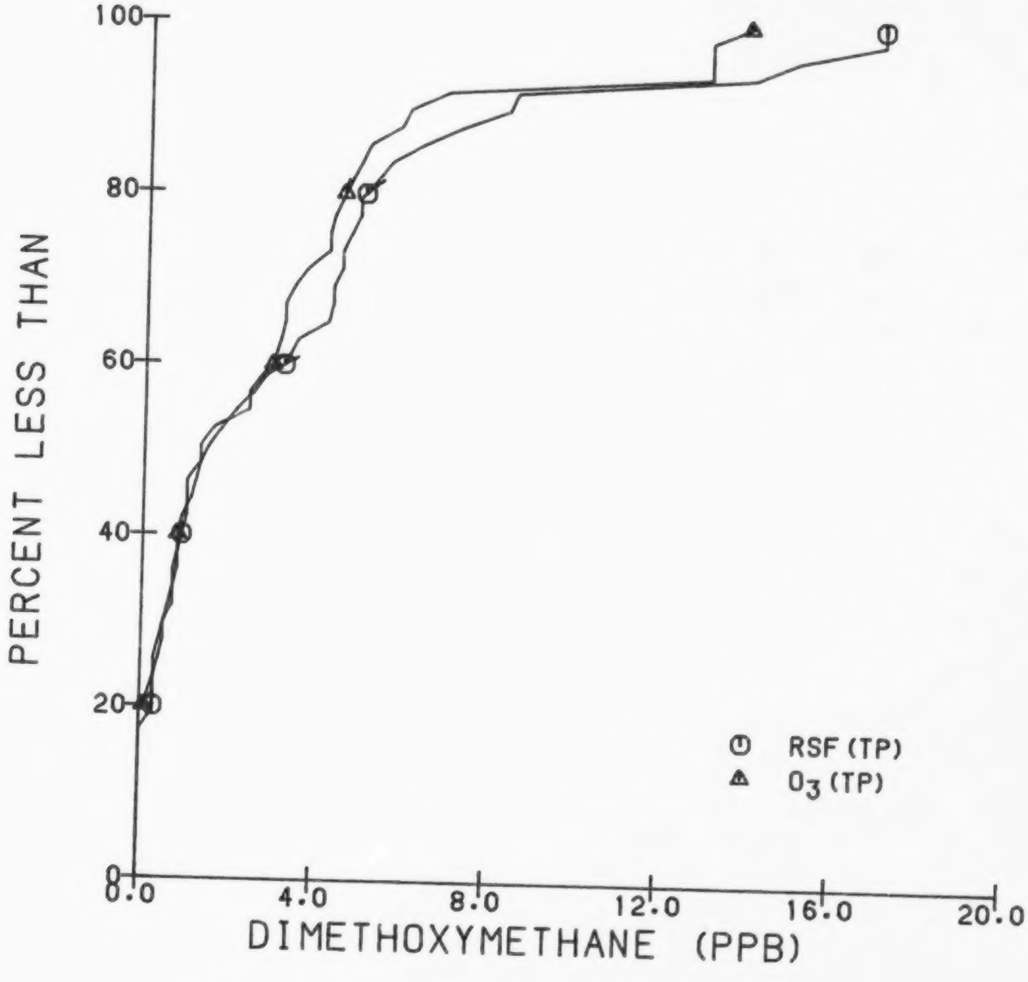

Figure 54. The effect of Torresdale Plant ozonation on dimethoxymethane levels (4/80 to 4/81).

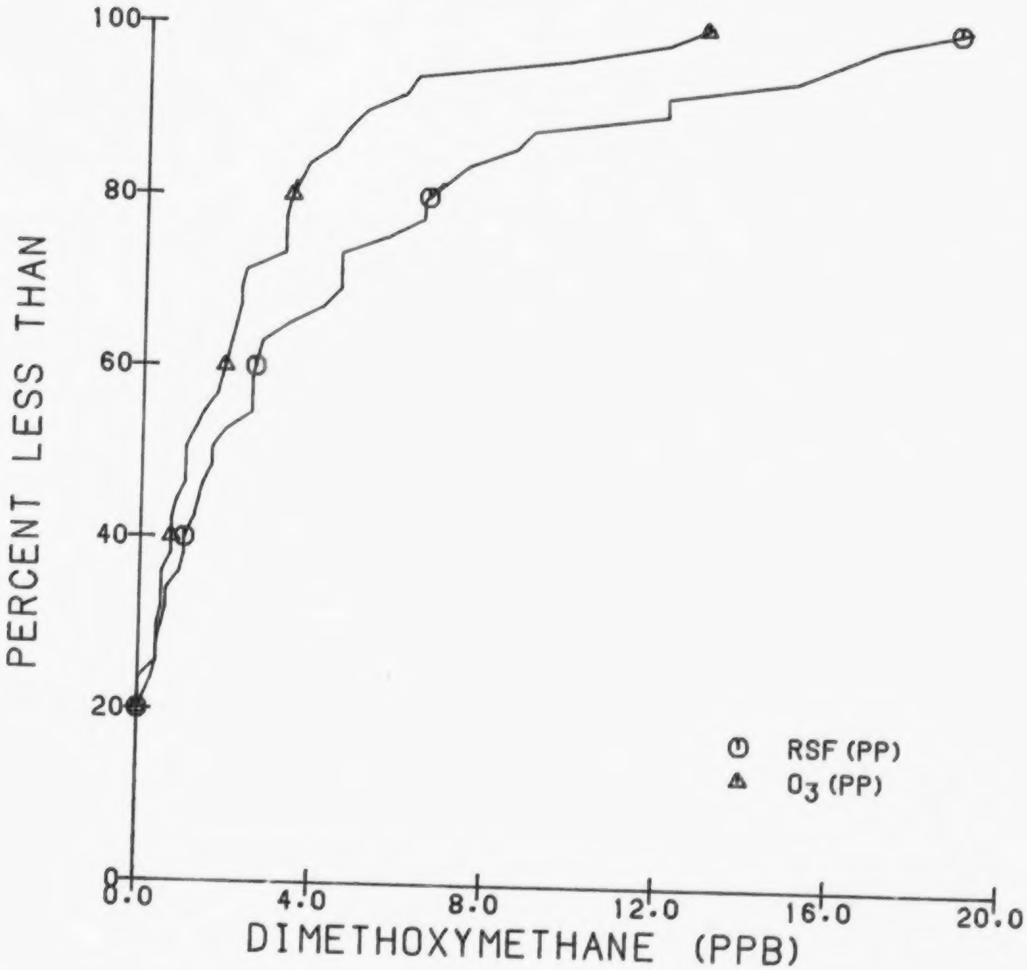

Figure 55. The effect of Pilot Plant ozonation on dimethoxymethane levels (4/80 to 4/81).

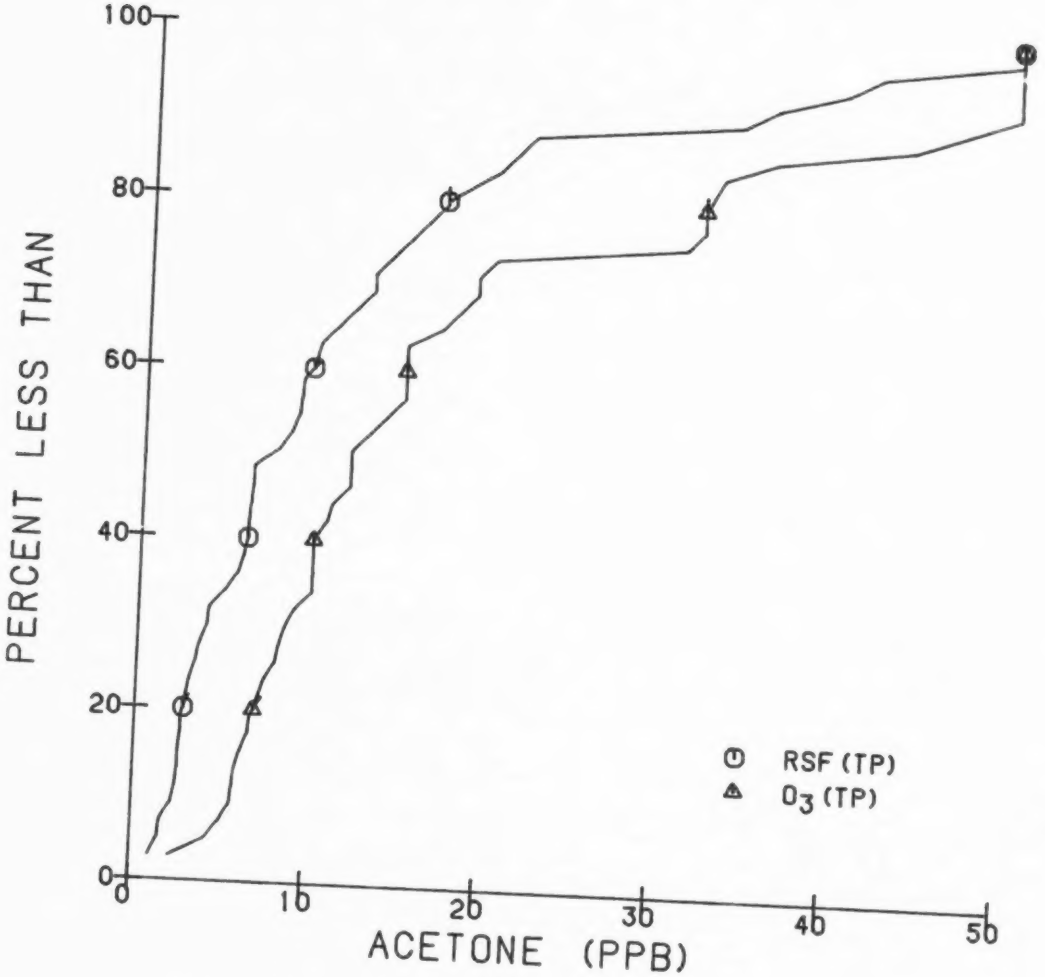

Figure 56. The effect of Torresdale Plant ozonation on acetone levels (4/80 to 4/81).

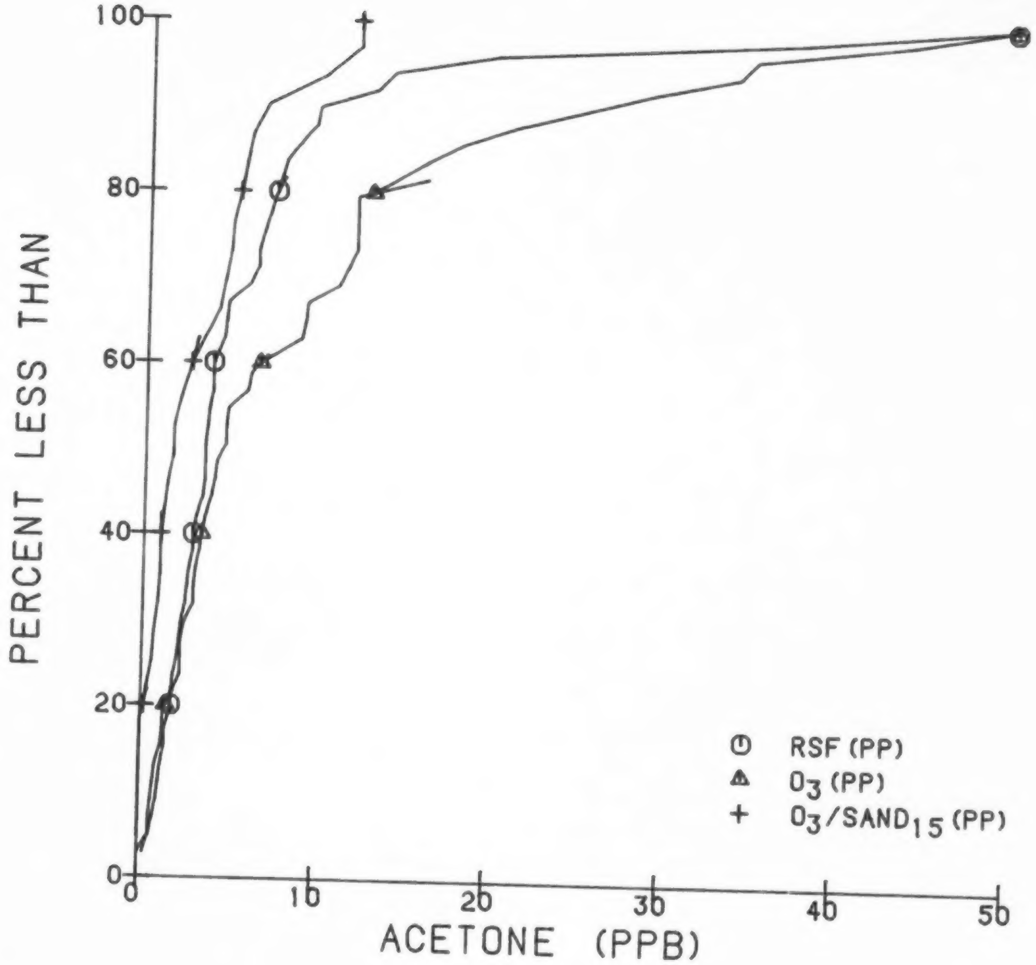

Figure 57. The effect of Pilot Plant ozonation on acetone levels (4/80 to 4/81).

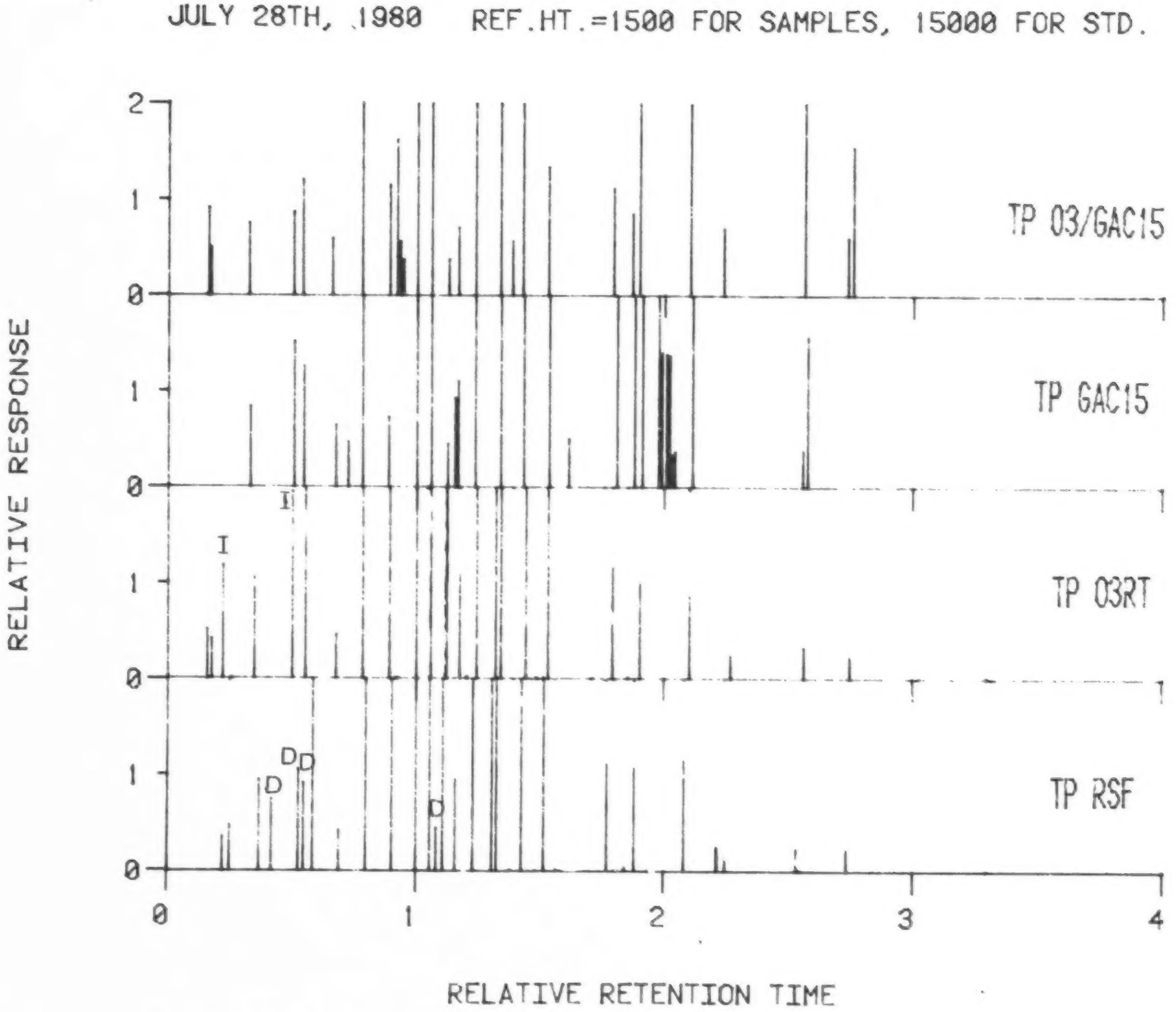

Figure 58. Spiked profiles of purgeable organics for the Torresdale Plant.

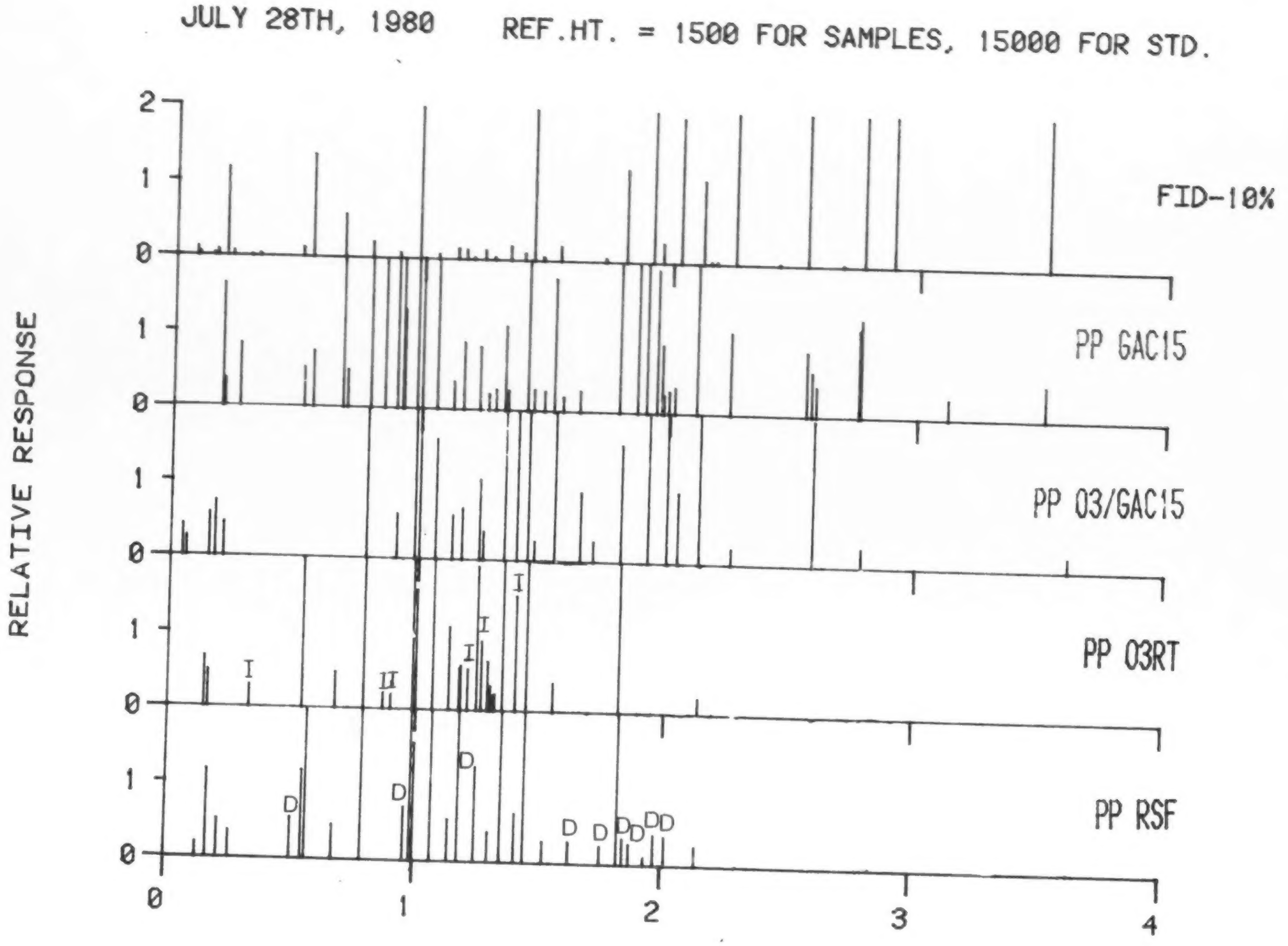

Figure 59. Spiked profiles of purgeable organics for the Pilot Plant.

process and the direction of that change. The variability of the number of peaks that change indicates that each sampling period is unique. The average number of peaks in a GC profile for the influent and effluent of the Torresdale ozone contactor is 25.8 ± 5.4. Approximately 15% of the peaks change by a factor of 2 or more during the ozonation process. Approximately 5% of the average number of peaks in the Torresdale samples increase indicating byproduct formation. Thus, 10% of the changes are attributed to aeration or oxidation. The Pilot Plant ozonator influent and effluent samples have 24.6 ± 6.8 peaks per profile. The average number of peaks for which response changed was 21% with 15% attributed to aeration or oxidation and 6% to byproduct formation.

TABLE 46. RESULTS OF VOLATILE ORGANIC ANALYSIS - OZONE CONTACTOR EFFLUENTS

	Halogenated	Ozonator Effluent			
		Torresdale Plant		Pilot Plant	
		Avg.	Range	Avg.	Range
P	Chloroform	46	16-110	2.8	0.2-26
P	Dichlorobromomethane	15	2.9-28	0.8	0.1-7.9
P	Dibromochloromethane	4.8	0.6-9.6	0.2	<0.1-2.3
P	Bromoform	0.3	<0.1-0.9	<0.1	<0.1-0.1
P	Methylene Chloride	0.3	<0.1-1.1	0.2	<0.1-1.5
P	1,2-Dichloroethane	1.3	<0.1-14	1.0	<0.1-7.3
P	1,1,1-Trichloroethane	0.1	<0.1-0.5	0.1	<0.1-0.4
P	Carbon Tetrachloride	0.2	<0.1-5.0	<0.1	<0.1-0.2
P	1,2-Dichloropropane	4.8	0.1-22	3.0	0.1-16
P	Trichloroethylene	0.4	<0.1-1.3	0.1	<0.1-0.4
P	1,1,2,2-Tetrachloroethylene	0.1	<0.1-0.8	0.1	<0.1-0.9
P	Chlorobenzene	0.1	<0.1	<0.1	<0.1
	Bis(2-chloroethyl) ether	<0.3	<0.1	<0.3	<0.1
	1,2-Dichlorobenzene	<0.1	<0.1	<0.1	<0.1

	Non-Halogenated	Ozonator Effluent			
		Torresdale Plant		Pilot Plant	
		Avg.	Range	Avg.	Range
	Acetone	21	2.3-100	9.4	2.2-67
	Dimethoxymethane	3.1	<0.1-14	2.3	<0.1-13
P	Benzene	0.2	<0.1-0.7	0.2	<0.1-0.6
P	Toluene	0.4	<0.1-1.0	0.2	<0.1-1.9
P	Ethylbenzene	<0.1	<0.1-0.4	<0.1	<0.1-0.3
	Cumene	0.1	<0.1-0.9	<0.1	<0.1-0.3
	o-Xylene	<0.1	<0.1-0.5	<0.1	<0.1-0.6
	m-Xylene	<0.1	<0.1-0.3	<0.1	<0.1-0.6

P - Priority Pollutant

TABLE 47 GC/MS IDENTIFICATION DATA[1]

COMPOUND	RRT[2]	4/15/80		7/14/80	7/28/80		9/22/80	
		O_3C(TP)	O_3RT(TP)	O_3RT(PP)	RSF(PP)	O_3RT(PP)	RSF(TP)	O_3RT(TP)
MECl	0.61	P(0.6)[3]	P(0.4)	-(BD)[4]	-(0.1)	-(BD)	P(0.1)	P(BD)
CHLO	1.00	P(63)	P(61)	P(1.4)	P(0.9)	P(1.4)	P(115)	P(73)
DCE2	1.06	-(0.2)	P(0.1)	P(2.5)	P(0.5)	P(2.3)	P(0.9)	-(0.7)
TCE1	1.17	P(BD)	-(BD)	-(BD)	-(0.1)	-(BD)	-(0.1)	-(BD)
CTET	1.19	-(BD)	-(BD)	-(BD)	-(BD)	-(BD)	-(0.3)	-(0.1)
DCBM	1.23	P(13)	P(13)	P(0.3)	-(0.1)	-(0.3)	P(37)	P(26)
DCP2	1.33	P(0.1)	P(0.1)	P(2.4)	P(3.7)	P(2.3)	P(2.0)	P(1.8)
TCE	1.40	P(0.2)	P(0.2)	-(0.2)	-(BD)	-(0.3)	-(0.2)	-(0.5)
DBCM	1.45	P(1.9)	P(1.6)	-(0.1)	-(BD)	-(0.1)	P(8.9)	P(7.5)
BROM	1.68	-(BD)	-(BD)	-(BD)	-(0.1)	-(BD)	-(0.5)	-(0.4)
PER	1.87	P(0.1)	-(0.1)	-(BD)	-(BD)	-(BD)	-(0.7)	-(0.1)
CBEN	2.07	-(BD)	-(BD)	-(BD)	-(BD)	-(BD)	-(1.3)	-(0.5)
ACET	0.66	P(7.5)	P(11)	-(3.2)	-(2.0)	-(9.1)	P(21)	P(44)
DMM	0.82	-(BD)	-(BD)	-(3.4)	-(6.4)	-(3.2)	-(0.5)	-(BD)
BEN	1.42	P(0.1)	P(0.1)	-(0.4)	-(0.3)	-(0.4)	-(0.2)	-(0.2)
TOL	1.98	P(1.2)	P(0.7)	-(0.2)	-(0.1)	-(0.5)	-(0.2)	-(BD)
EBEN	2.24	-(0.2)	-(0.1)	-(BD)	-(BD)	-(BD)	-(BD)	-(BD)
THF	0.92	T	-	-	-	-	-	-
ET$_2$O	0.98	T	-	-	-	-	-	T
MEK	1.04	-	T	-	-	-	-	-

1. Analysis performed on a Finnigan 4021 GC/MS/DS. Mass Range Scanned: 33-300 amu. Scan Rate: 33-300 amu/1.95 second.

2. Relative retention time versus chloroform (absolute retention time of 15.9 minutes) using an 8 ft x 2mm ID glass column packed with 1% SP-1000 on Carbopack B (60/80 Mesh). Carrier gas: Helium at 20 mL/min. Oven Program: 45°C (4 minute hold) to 220°C at 6°C/min.

3. The number in parenthesis is the quantified value by GC analysis.

4. BD is below detectable limits. For GC/MS analysis this will vary due to daily sensitivity fluctuations from 0.1 to 1.0 ppb for all compounds except for ACET and DMM where it varies from 5 to 10 ppb.

T = tentitive identification - GC/MS only.
P = positive identification - GC/MS and GC retention time.

THF - Tetrahydrofuran
ET$_2$O - Ethyl ether
MEK - Methyl ethyl ketone

TABLE 47 (con't) GC/MS IDENTIFICATION DATA[1]

COM-POUND	RRT[2]	10/6/80	11/10/80		1/13/81	9/29/81	10/6/81
		O_3/GAC(PP)	RSF(PP)	O_3RT(PP)	O_3RT(TP)	RSF(PP)	O_3RT(PP)
MECL	0.61	P(0.1)[3]	P(0.2)	P(0.1)	P(0.3)	P(0.1)	P(0.4)
CHLO	1.00	P(7.3)	P(1.9)	P(1.7)	P(17)	P(2.6)	P(2.2)
DCE2	1.06	P(0.9)	P(1.1)	P(1.0)	P(3.9)	P(1.0)	P(0.5)
TCE1	1.17	P(0.1)	P(0.1)	P(0.1)	P(0.1)	-(0.1)	P(0.2)
CTET	1.19	-(0.1)	-(BD)[4]	-(BD)	P(0.3)	-(BD)	P(0.3)
DCBM	1.23	P(1.0)	P(0.6)	P(0.6)	P(6.5)	P(0.9)	P(1.1)
DCP2	1.33	P(1.1)	P(6.9)	P(5.2)	P(22)	P(1.8)	P(1.3)
TCE	1.40	-(BD)	P(0.3)	-(0.1)	P(0.6)	P(0.2)	-(0.2)
DBCM	1.45	-(BD)	-(0.2)	-(0.2)	P(2.1)	-(0.3)	P(0.4)
BROM	1.68	-(BD)	-(BD)	-(BD)	-(0.2)	-(BD)	-(BD)
PER	1.87	-(0.1)	P(BD)	-(BD)	P(0.3)	P(0.2)	P(0.3)
CBEN	2.07	-(BD)	P(1.3)	P(0.3)	P(0.3)	-(BD)	P(0.3)
ACET	0.66	P(0.8)	-(1.7)	P(12)	P(100)	P(3.9)	P(89)
DMM	0.82	-(2.2)	T(15)	T(9.7)	-(1.1)	-(8.9)	T(3.5)
BEN	1.42	P(0.1)	P(0.1)	P(0.1)	P(0.7)	-(4.0)	P(1.5)
TOL	1.98	P(BD)	P(0.1)	P(BD)	P(1.9)	-(0.5)	P(0.3)
EBEN	2.24	-(BD)	-(BD)	-(BD)	P(0.2)	-(BD)	P(BD)
THF	0.92	-	-	-	-	-	-
ET_2O	0.98	-	-	-	T	-	T
MEK	1.04	-	-	-	-	-	-

1. Analysis performed on a Finnigan 4021 GC/MS/DS. Mass Range Scanned: 33-300 amu. Scan Rate: 33-300 amu/1.95 second.

2. Relative retention time versus chloroform (absolute retention time of 15.9 minutes) using an 8 ft x 2mm ID glass column packed with 1% SP-1000 on Carbopack B (60/80 Mesh) Carrier gas: Helium at 20 mL/min. Oven Program: 45°C (4 minute hold) to 220°C at 6°C/min.

3. The number in parenthesis is the quantified value by GC analysis.

4. BD is below detectable limits. For GC/MS analysis this will vary due to daily sensitivity fluctuations from 0.1 to 1.0 ppb for all compounds except for ACET and DMM where it varies from 5 to 10 ppb.

T = tentitive identification - GC/MS only.
P = positive identification - GC/MS and GC retention time.

THF - Tetrahydrofuran
ET_2O - Ethyl ether
MEK - Methyl ethyl ketone

TABLE 48. FLAME IONIZATION DETECTOR RESPONSE OF THE CHANGES OF PURGEABLE ORGANICS ACROSS THE OZONATION PROCESS

	Change in The Number of Peaks			
	Pilot Plant		Torresdale Plant	
Sample Date	Increase	Decrease	Increase	Decrease
5/5/80	-	-	0	0
5/12/80	-	-	0	2
5/20/80	-	-	1	6
5/27/80	-	-	0	0
6/2/80	-	-	0	5
6/9/80	2	0	2	0
6/17/80	3	3	-	-
6/23/80	0	1	6	3
6/30/80	0	3	-	-
7/21/80	1	9	-	-
7/28/80*	6	9	2	4
9/2/80	1	5	-	-

	PP	TP
Total # Peaks (Avg)	24.6 ± 6.8	25.8 ± 5.4
% Increase upon O_3	5%	5%
% Decrease upon O_3	15%	10%

*Shown in Figures 59 and 60.
-Samples not analyzed.
All changes are greater than a factor of two.

The quantitative data has shown that acetone increases while 1,2-dichloropropane and the trihalomethanes decrease. However, these compounds do not change by a factor of two. Thus, the estimates presented are conservative in that they only show dramatic changes. GC/MS analysis indicated that methyl ethyl ketone (MEK) (tentative) and acetone were purgeable byproducts of ozonation (see Table 47).

Semi-Volatiles - MRR Analysis -- The semi-volatile matrix of organics was evaluated before and after ozonation in the Torresdale and Pilot Plants to observe if any changes occurred. Figures 60 and 61 show examples of the GC profiles from the influent and effluent of the Torresdale and Pilot Plant ozonation processes (from C8 to C26 inclusive). Table 48 showed the corresponding GC/MS analysis of the RSF effluent from each plant for the GC profile of Figure 60 and 61. Table 44 showed the average peak distributions for the Pilot Plant and Torresdale Plant rapid sand filter effluents for ten sampling periods.

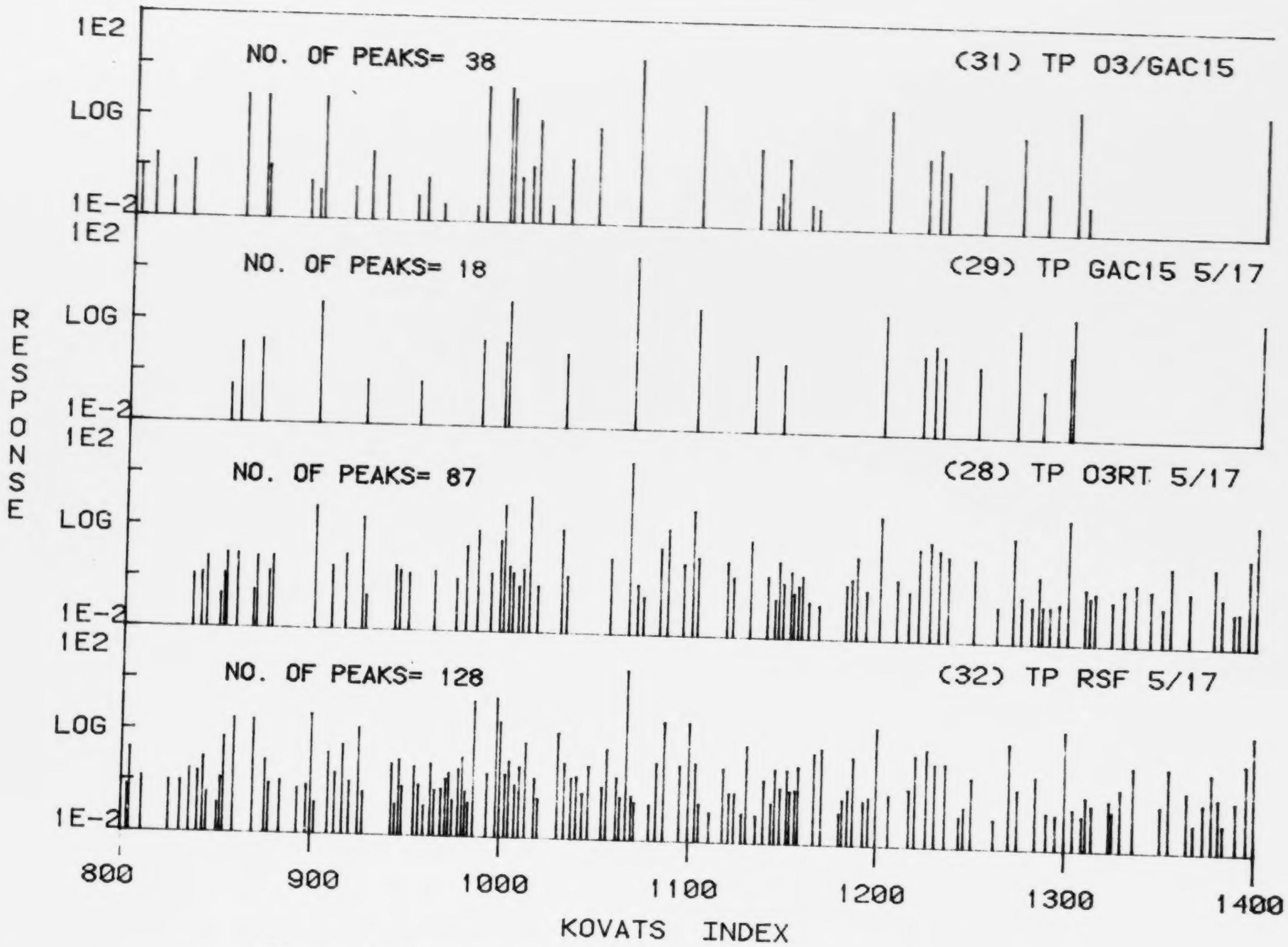

Figure 60a. Non-polar organic compounds in the Torresdale Plant.

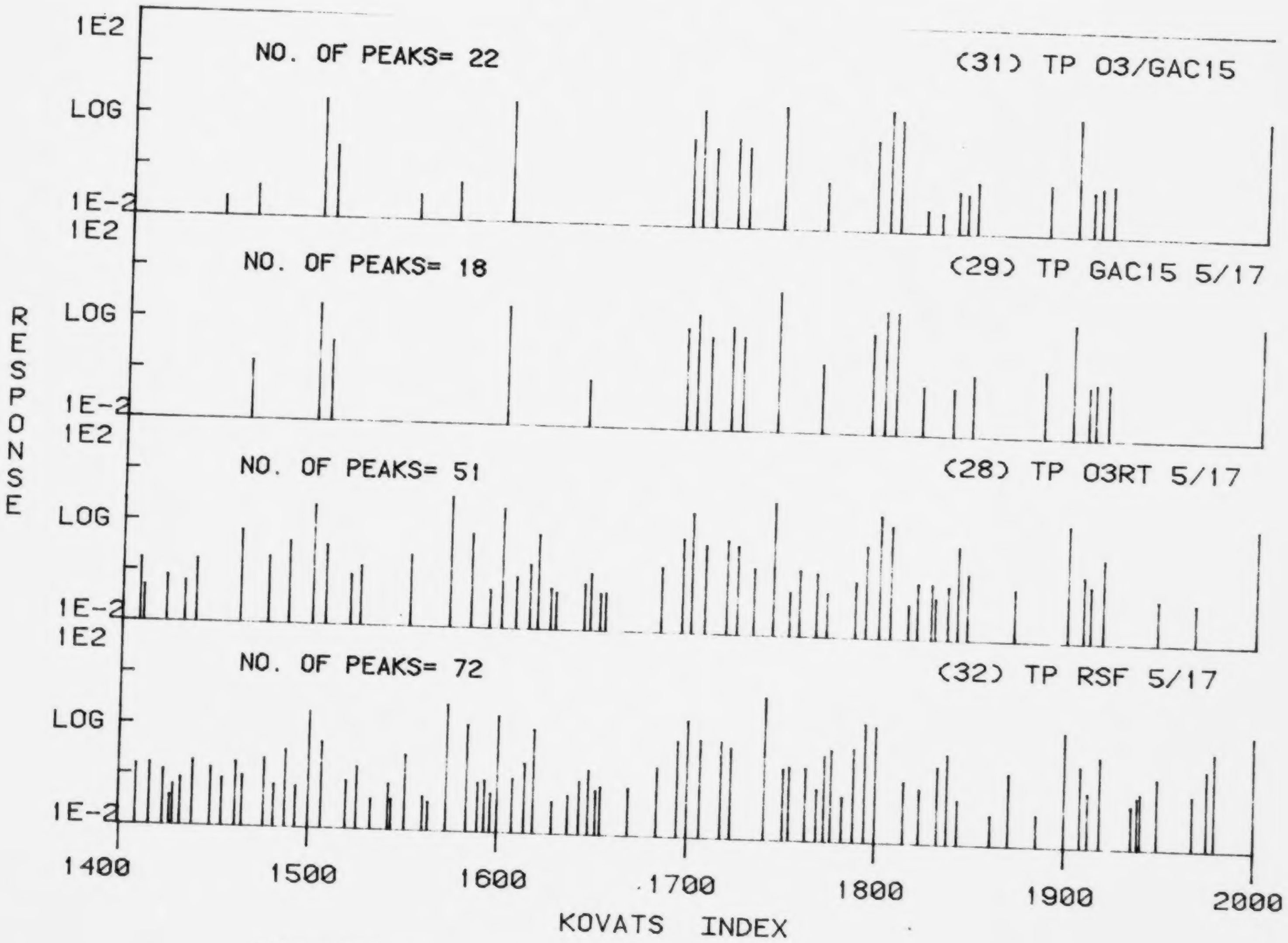

Figure 60b. Non-polar organic compounds in the Torresdale Plant.

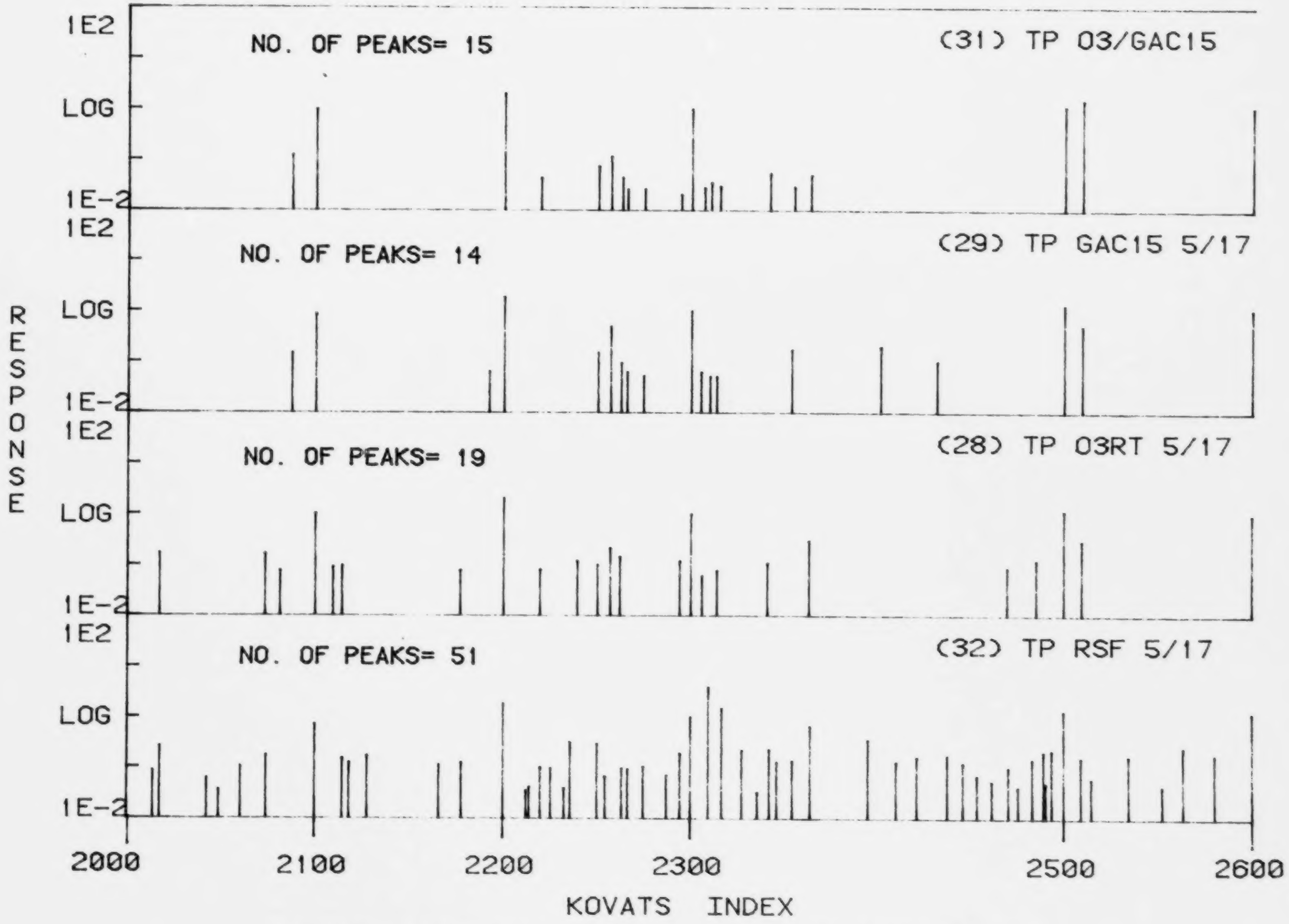

Figure 60c. Non-polar organic compounds in the Torresdale Plant.

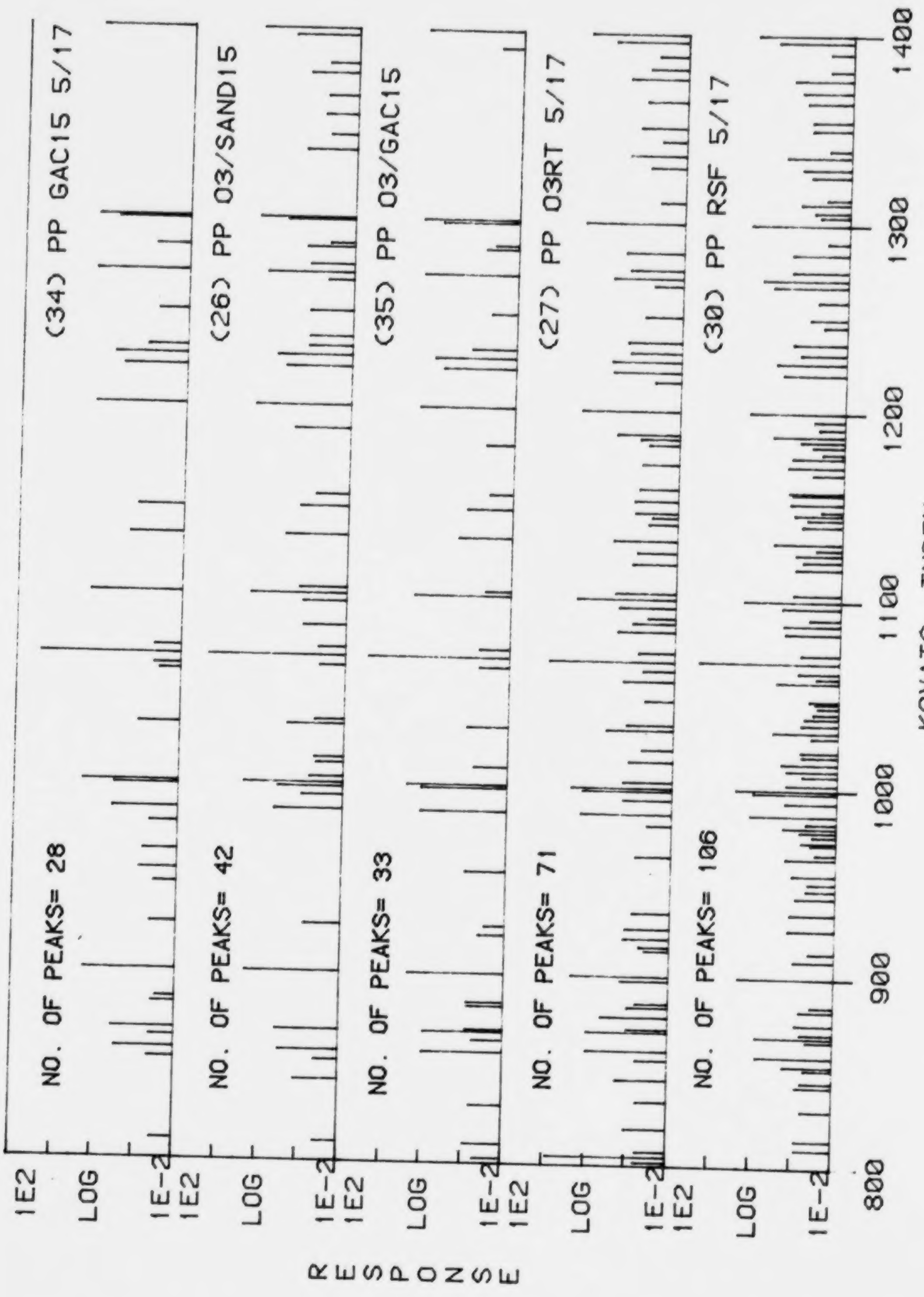

Figure 61a. Non-polar organic compounds in the Pilot Plant.

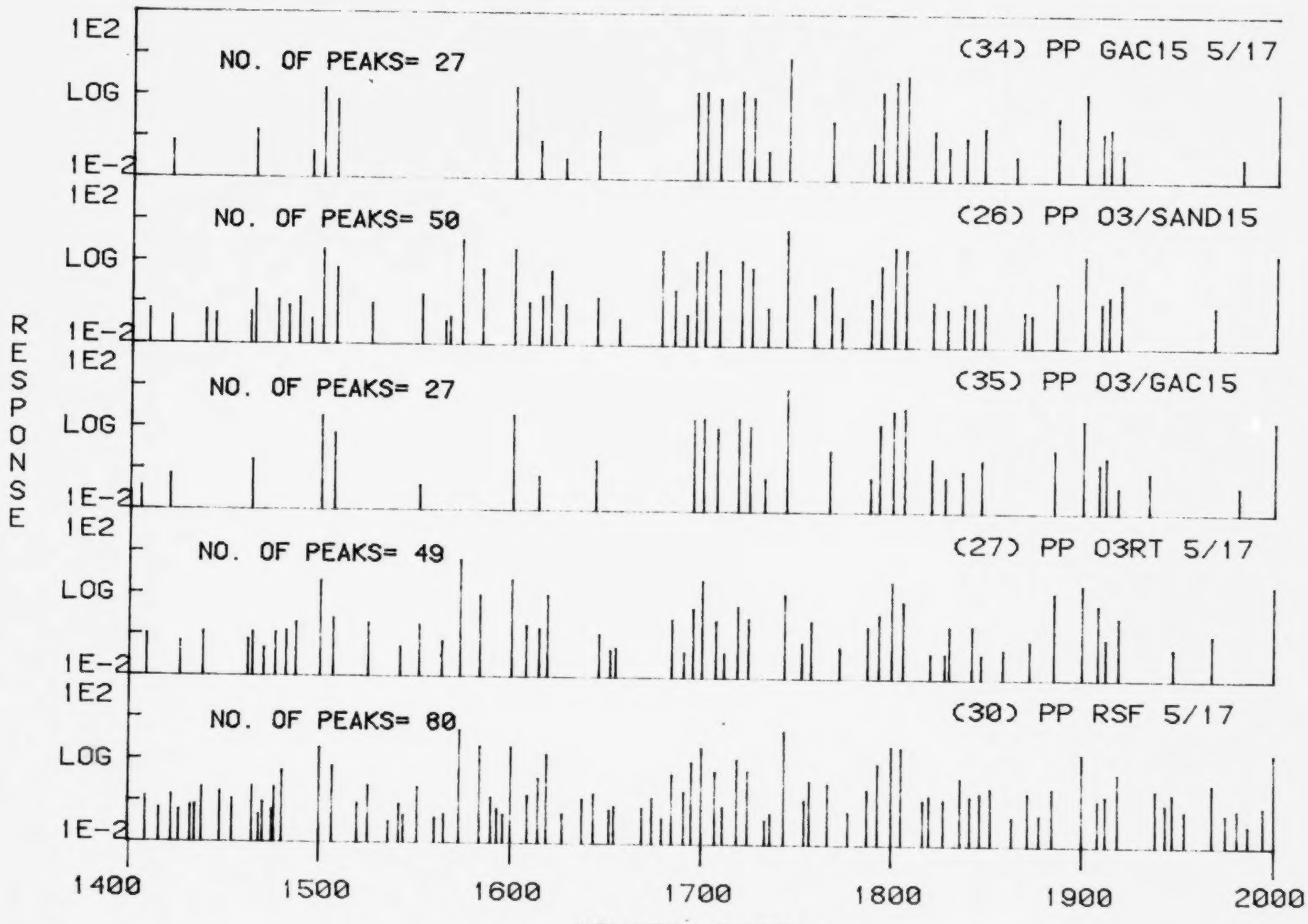

Figure 61b. Non-polar organic compounds in the Pilot Plant.

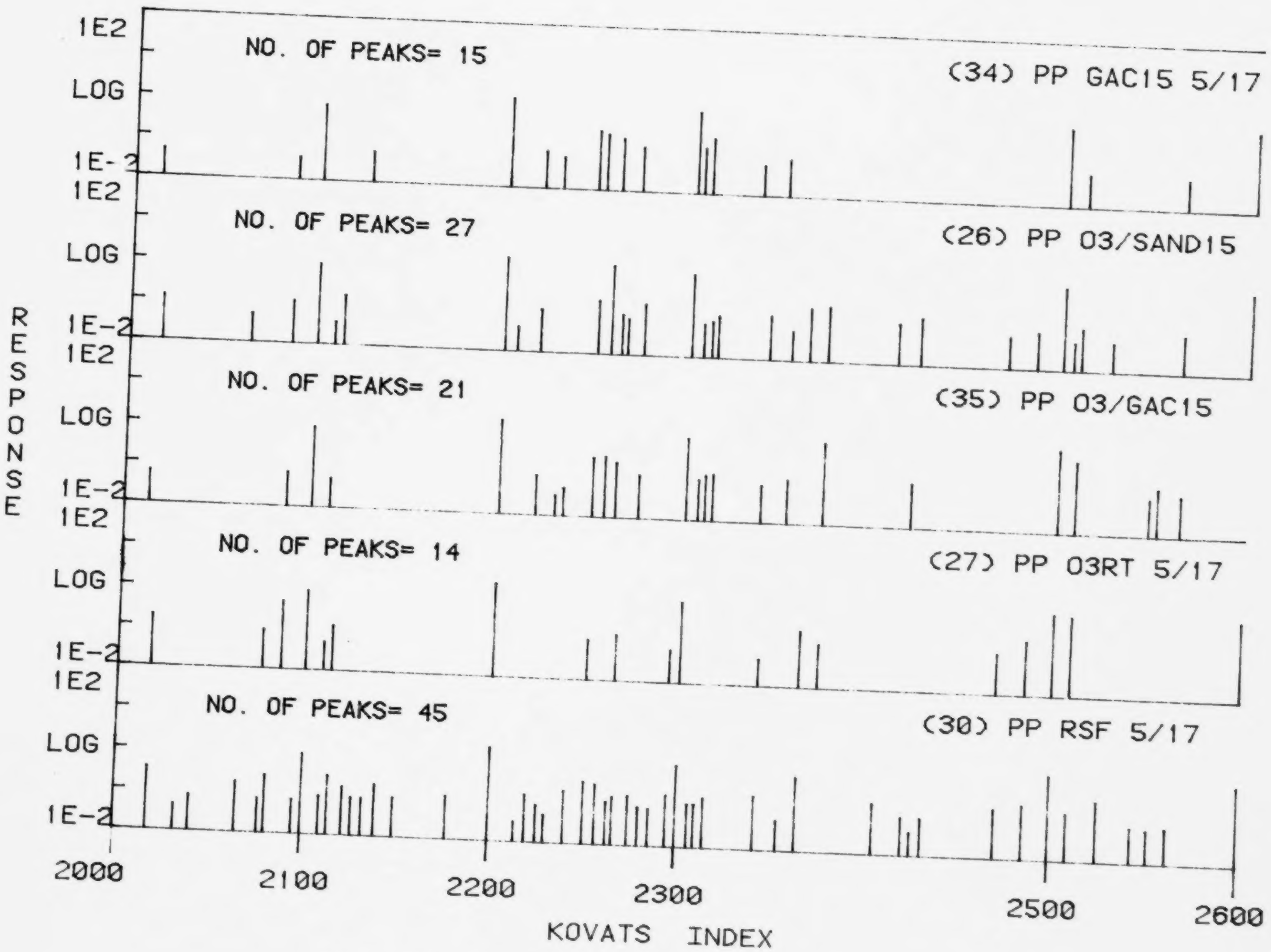

Figure 61c. Non-polar organic compounds in the Pilot Plant.

A series of statistical comparisons were completed on each set of ozonator influent and effluent GC profiles using Chi-square contingency tables. The null hypothesis is that the samples in and out of the ozonator are homogeneous. Those sampling periods whose Chi-square value exceed the critical value at P=0.05 and 14 degrees of freedom were determined. This analysis shows that the Pilot Plant and Torresdale Plant have 6 of 9 and 8 of 10 periods, respectively, where the ozonator has a significant effect on the organic matrix.

An evaluation of the mechanism responsible for the observed differences was undertaken. Stripping of trace organics will primarily affect the low molecular weight compounds (168), as shown in Figure 62. However, when oxidation of organics occurs, the MRR broad spectrum GC profile analysis would tend to show this as missing peaks, because the analytical technique is not designed to be sensitive to polar organic compounds. Thus, if oxidation was the primary cause for the difference found by Chi-square analysis for the ozonation process, the changes in the chromatograms would be distributed over the entire C8-C26 hydrocarbon range (Kovat Indices 800-2600). Removing the lower MW compounds should remove the effect of stripping. The resulting Chi-square values and the associated critical value with removal of C8-C11 hydrocarbons ($800 < KI < 1100$) were thus compared.

The result of the Chi-square analysis for the Pilot Plant (non-chlorinated) show a significant effect (P=0.05) caused by the ozonation unit process for six out of nine sampling periods. Four remain significant (at P=0.05) when the volatile organics ($800 < KI < 1100$) are removed. Thus, oxidation is the dominant mechanism taking place in the Pilot Plant ozonator during four of the six sampling periods where a significant change between influent and effluent were found.

For the Torresdale Plant, eight of the ten samples show significant effects at (P=0.05) for the ozonation process. Three remain significant when the volatiles ($800 < KI < 1100$) were removed. This shows that oxidation is dominant. Aeration was dominant for the other five. Thus both mechanisms are operative and dominance changes with time. This indicates that a variable influent of trace organics is present and that each sampling period must be considered unique.

Figure 63 shows the effect of ozonation on the nonpolar trace organics with Kovats Indices between 800 and 1400, collected by the MRR method from the Pilot and Torresdale Plants. The Torresdale Plant influent contained a larger concentration of trace organics than the Pilot Plant. Aeration and oxidation apparently reduced 33% of the total area of the peaks in the influent during ozonation at Torresdale. The Pilot Plant ozone contactor influent had total concentrations of the trace organics about 50% lower than the Torresdale Plant. No apparent changes were observed due to the ozonation process at the Pilot Plant. Figure 59 shows the GC profiles corresponding to week 5 at the Pilot Plant which confirms the observations in Figure 63. The only compound tentatively identified by GC/MS to be found only in the ozonator effluent was a cis or trans isomer of 2,5-dimethyl tetrahydrofuran.

A test for homogeneity of the influents to the two ozonation treatment

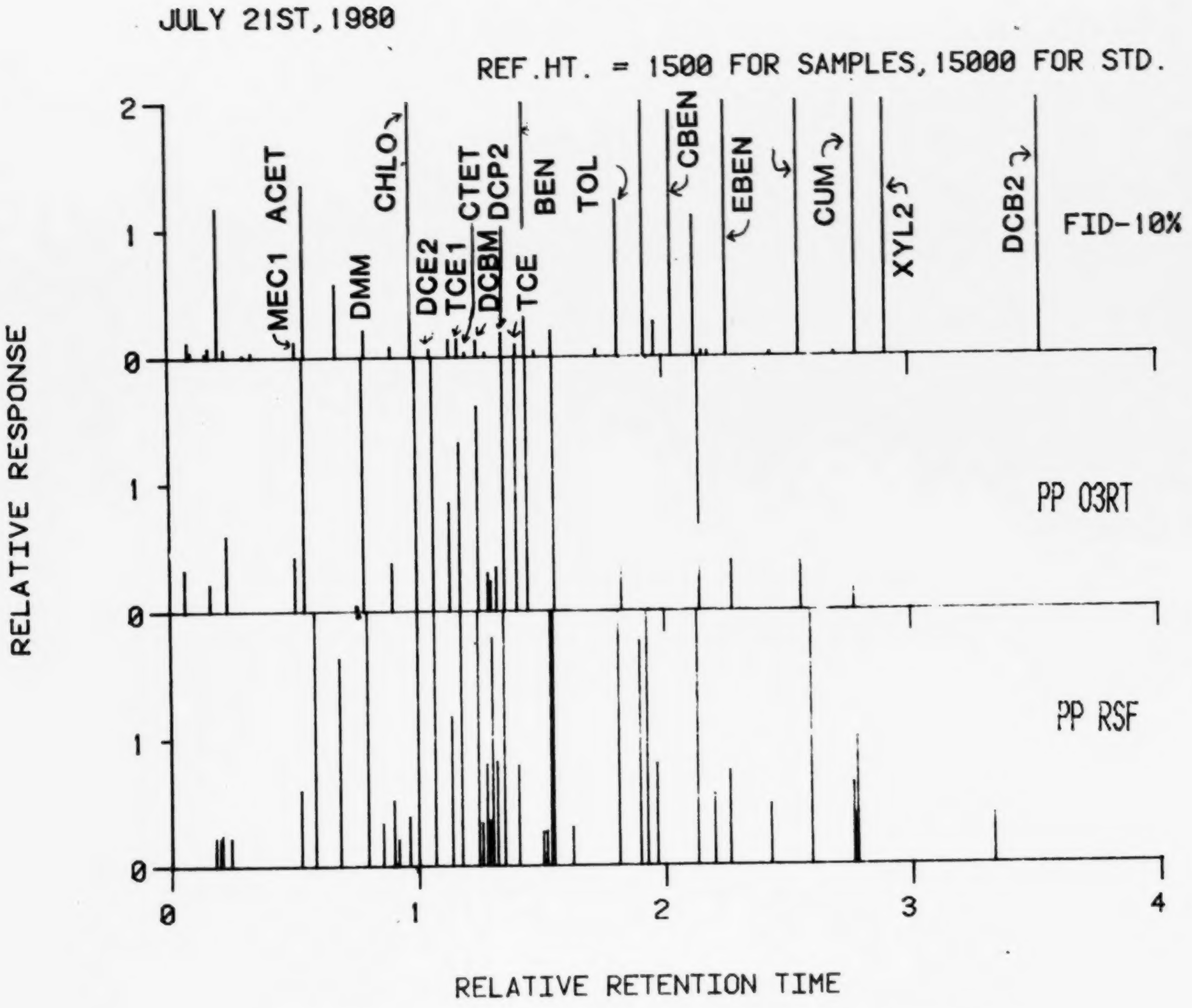

Figure 62. Purgeable organic profiles for the Pilot Plant.

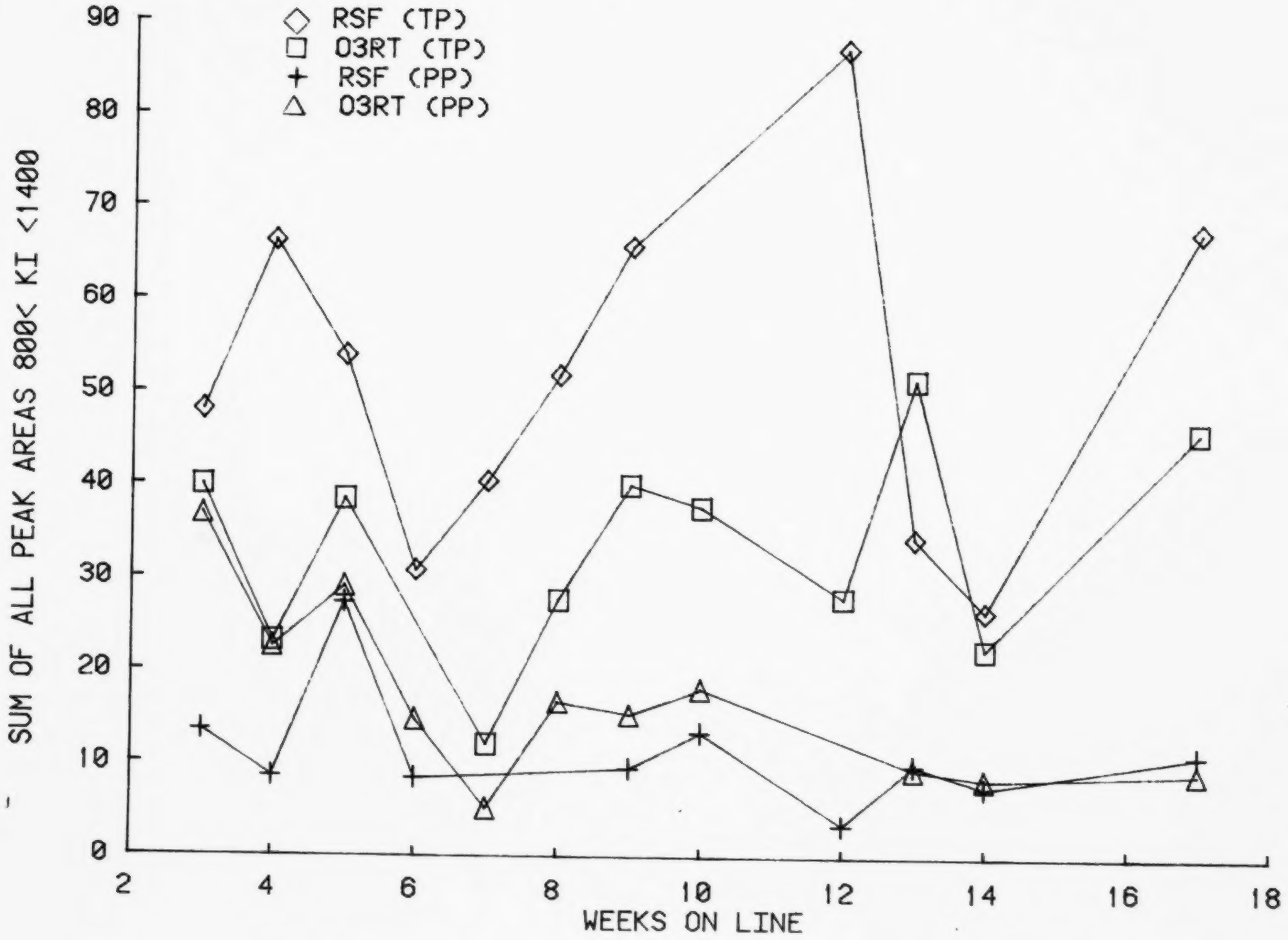

Figure 63. The effect of ozonation on non-polar organics (800<KI<1400) in the rapid sand filter effluents.

processes (separately) over many sampling periods was completed. Both influents were not homogeneous at P=0.05. This statistically confirms previous Pilot Plant runs at Torresdale which indicated variability of trace organic loading at ng/L concentrations (1,34,38). However, if all sampling periods for the effluent of the Pilot Plant are averaged and compared to the average for the Torresdale Plant, Chi-square does not indicate significant differences between the two plants. The arithmetic averaging of all the sampling periods contingency is the same as physically compositing the samples over the longer period of time. This may indicate, that if one composited the same amount of water (150 liters) for a period of time longer than 72 hours but shorter than 3 months, the differences that were observed in the semi-volatile organics trains may be removed.

The impact of the above statistical tests is to make questionable any semi-volatiles comparisons of ozonator performance between treatment trains. However, performance comparisons of carbon contactor effluents between the two sources of water within two sampling periods are possible because the adsorption mechanism accumulates the trace organic compounds over time and short term differences tend to be smoothed out.

Adsorption Systems --

The rapid sand filter and ozone contactor effluents were next applied to GAC adsorption systems. These systems were carefully monitored for both general and specific organic parameters. This information was used to determine the bed life of the respective adsorption systems based on various effluent criteria. Since the regeneration of carbon may account for up to 75% of the operating and maintenance costs associated with GAC treatment (2), increasing carbon bed life was considered as the primary means of achieving a decrease in the cost of GAC treatment.

The greatest difficulty in interpreting the relative effectiveness of GAC systems is in defining their useful bed life. Table 1 presented a priority listing of chemical groups in terms of their human health effects. This prioritization provides a protocal for screening the trace organic compounds and is an important consideration in the design of a GAC facility. In the following section, a large data base is presented so as to provide general information on the effectiveness of GAC for each of the groups listed.

The results in this section were again divided between those of the general organic parameters (DOC and THMFP) and those of the more specific organics. The effect of DOC on the adsorbability of the more harmful organics will be carefully evaluated. Emphasis has also been given to the volatile organic parameters of DCP and the trihalomethanes, since they are the primary halogenated organic compounds found in the Delaware River and the Torresdale rapid sand filter effluent, respectively. Acetone is also examined since it is the only compound positively identified as a by-product of the ozonation process. Lastly, results from the other volatiles and semi-volatiles are presented to provide an overall picture of the adsorbability of the medium weight organics.

Dissolved Organic Carbon (DOC) -- DOC levels through the Torresdale and Pilot Plant adsorption systems are presented in Figures 64 to 67. Figures 68 to 71 present the same results in terms of percent removal. The effluent curves all exhibit a breakthrough pattern typical of carbon adsorption systems used in the water treatment industry which is characterized by its three phases of breakthrough (36,38-41,44,45). In the initial phase, all but 5% to 15% of the applied DOC is removed by the carbon bed. The adsorptive mechanisms are so strong during this phase that those organics which are not removed may be considered nonadsorbable and nonbiodegradable. During the second phase of breakthrough, the adsorptive forces slowly diminish and there is a gradual rise in the effluent DOC concentration. Steady-state removal constitutes the third and final phase of breakthrough. Removal of organics during this phase is largely dependent on the biodegradability of the organics in the applied water since the adsorptive forces have only a minimal effect on the trace organics. Steady-state conditions were observed after 7 to 8 months of system operation (for the 15 minute EBCT systems) and continue throughout the remainder of the study. Removal of organics during this final phase of breakthrough ranged from 19% to 36%.

Table 49 presents the time each adsorption system remained in the initial phase of breakthrough. The duration of the initial phase has been defined for the purposes of this presentation to be the time until 400 ppb DOC appears in the effluent of the carbon system. When this effluent limit is reached, actual breakthrough (i.e. breakthrough of organics normally adsorbable on a virgin GAC bed) was considered to have begun. The results shown in Table 49 indicate that preozonation does not result in any significant increase in the time to initial DOC breakthrough. Since the primary role of preozonation was to produce biodegradable organics, the results reinforce our understanding that biodegradation plays only a relatively small role during the early stages of GAC column operation. A comparison of the 15 and 30 minute EBCT systems shows that the time to initial breakthrough for the 30 minute systems is approximately double that found for the comparable 15 minute systems, indicating that contact time is directly proportional to the time until initial DOC breakthrough. This confirms previous data at Torresdale on GAC (37).

Table 49 also shows that the Pilot Plant systems remained in the initial phase of breakthrough at least twice as long as the comparable Torresdale Plant systems. An explanation for this is offered in Table 50 which shows the cumulative DOC loading applied to the carbon bed (mg DOC/gm GAC) up to the time of breakthrough. While the rate of organic loading (especially chlorinated organic loading) was considerably less onto the Pilot Plant adsorption systems than onto the Torresdale Plant systems, the data shows that nearly twice the cumulative DOC loading (at breakthrough) was realized through the Pilot Plant systems. These results indicate the importance of removing as much DOC as possible from the process stream prior to carbon application. Although preozonation and empty bed contact time did not significantly affect the maximum DOC loading which may be applied to a GAC bed prior to initial breakthrough, pretreatment did have a significant effect.

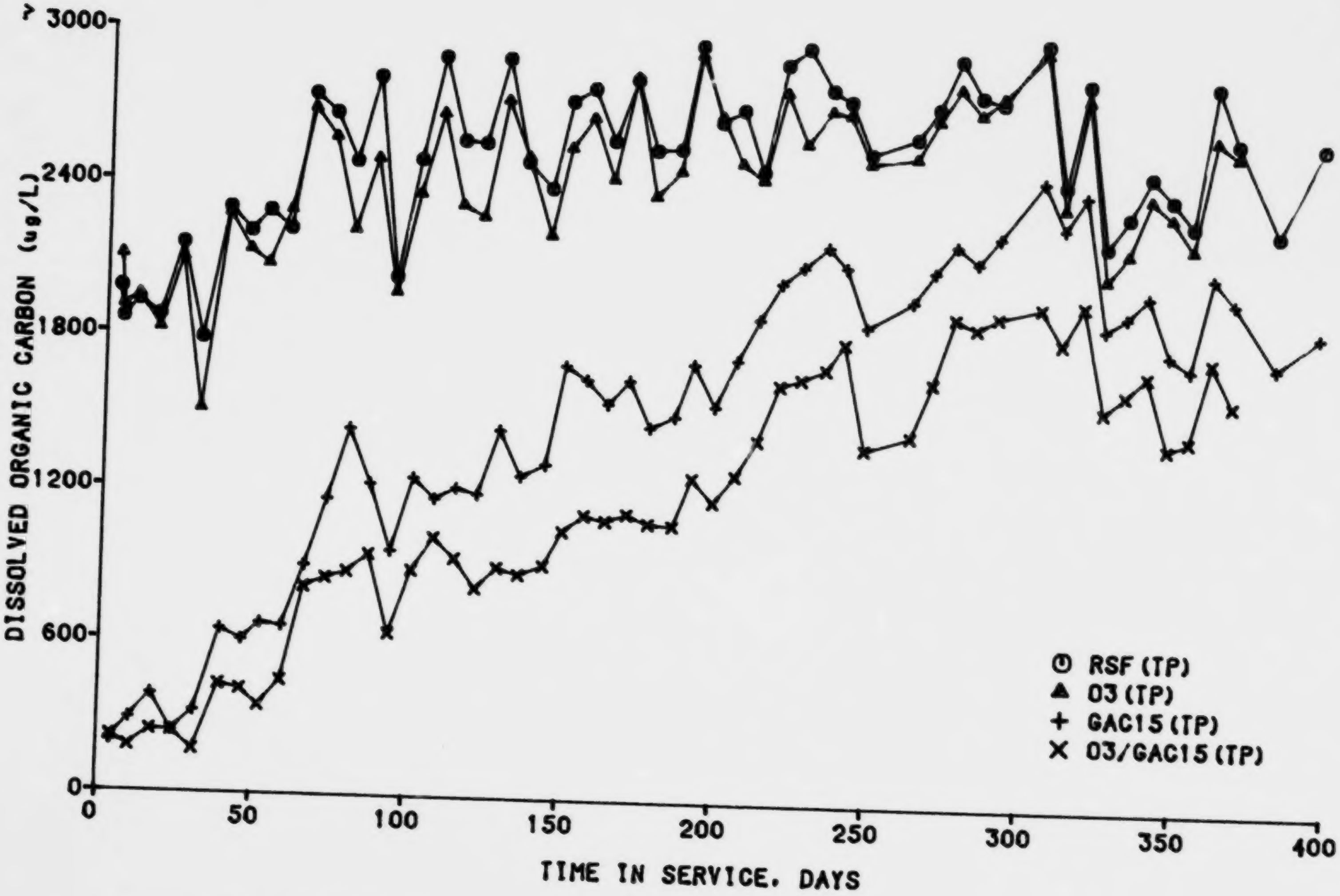

Figure 64. DOC levels through the Torresdale Plant adsorption systems (15 min. EBCT).

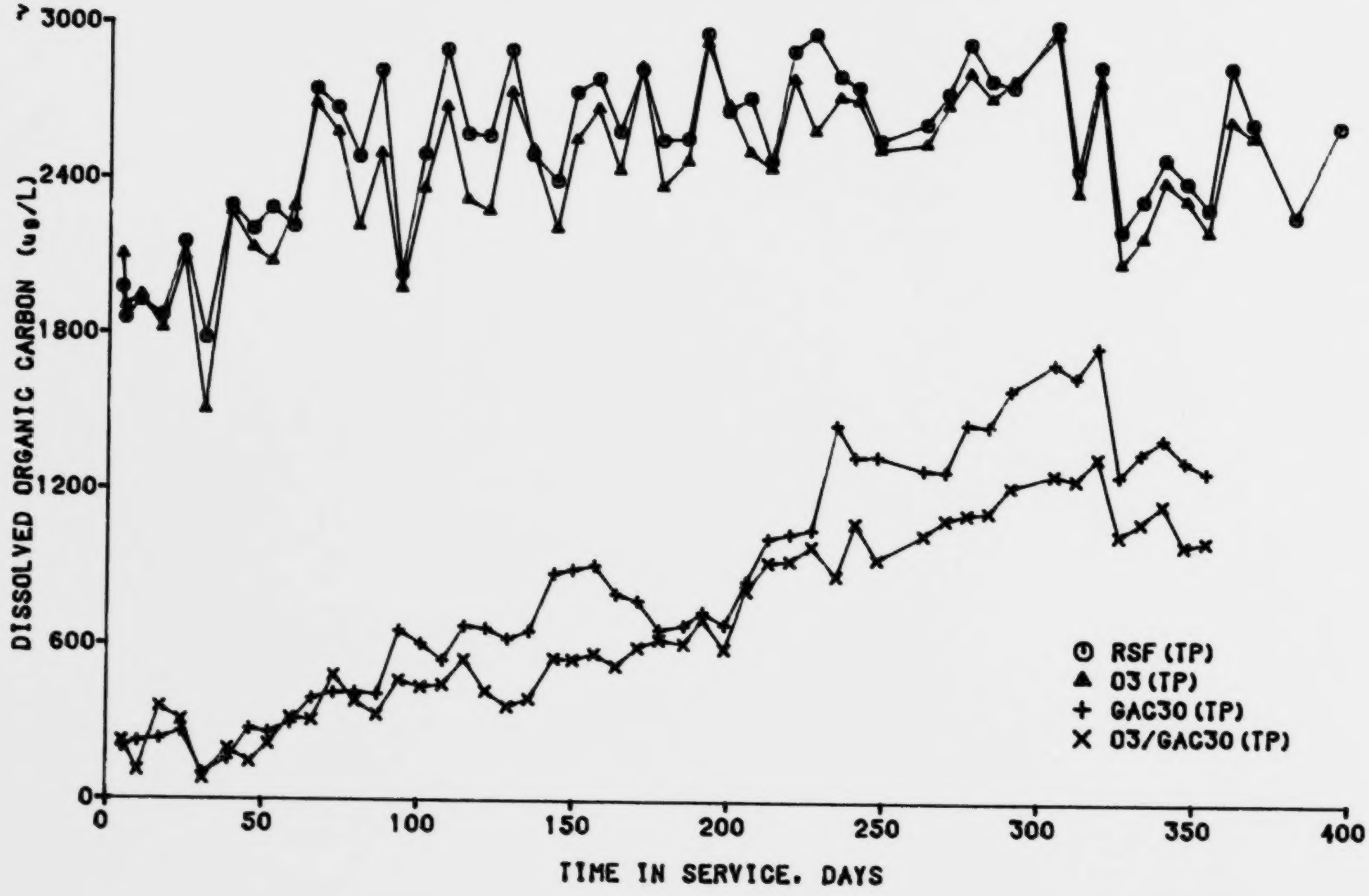

Figure 65. DOC levels through the Torresdale Plant adsorption systems (30 min. EBCT).

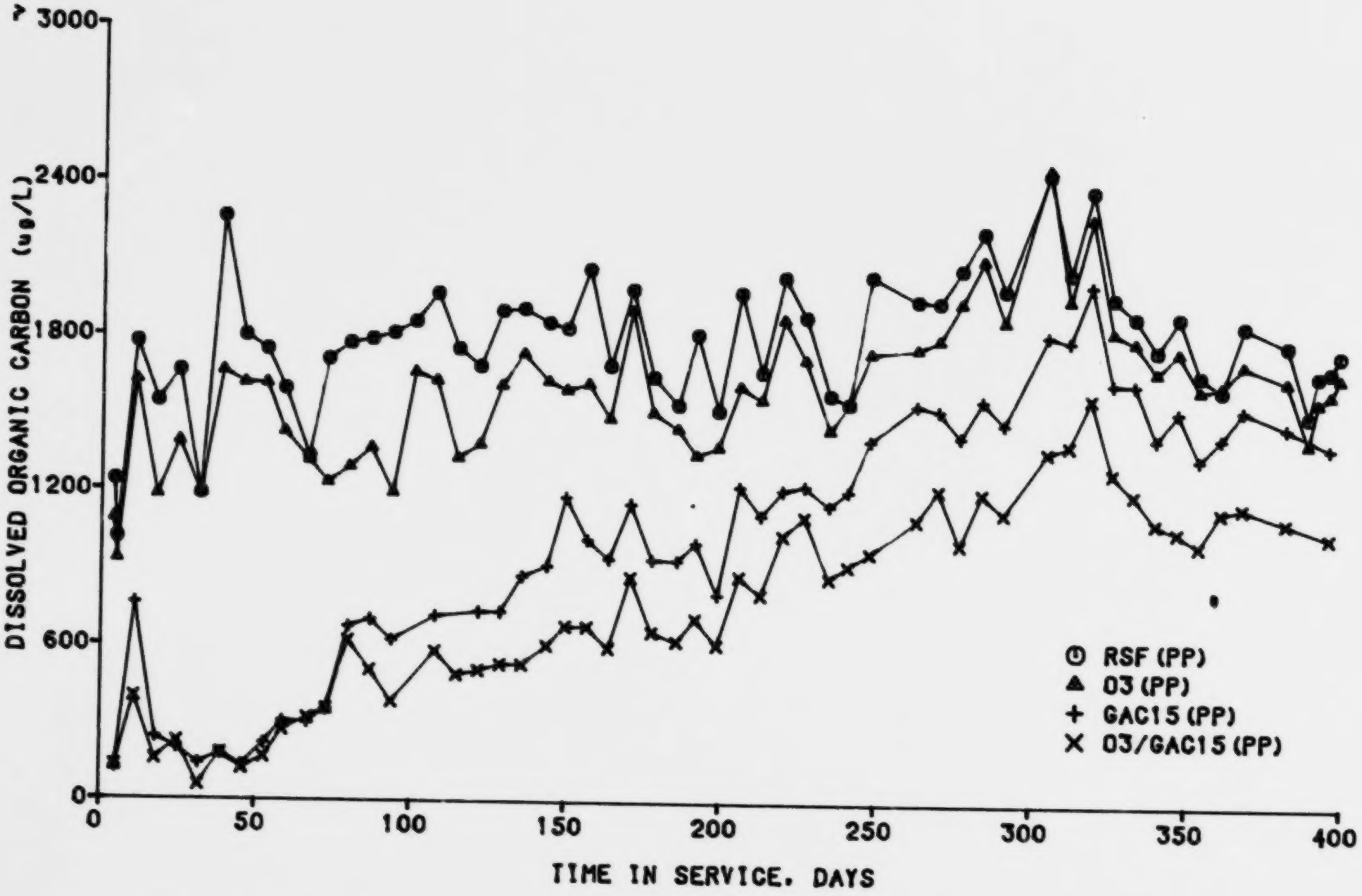

Figure 66. DOC levels through the Pilot Plant adsorption systems (15 min. EBCT).

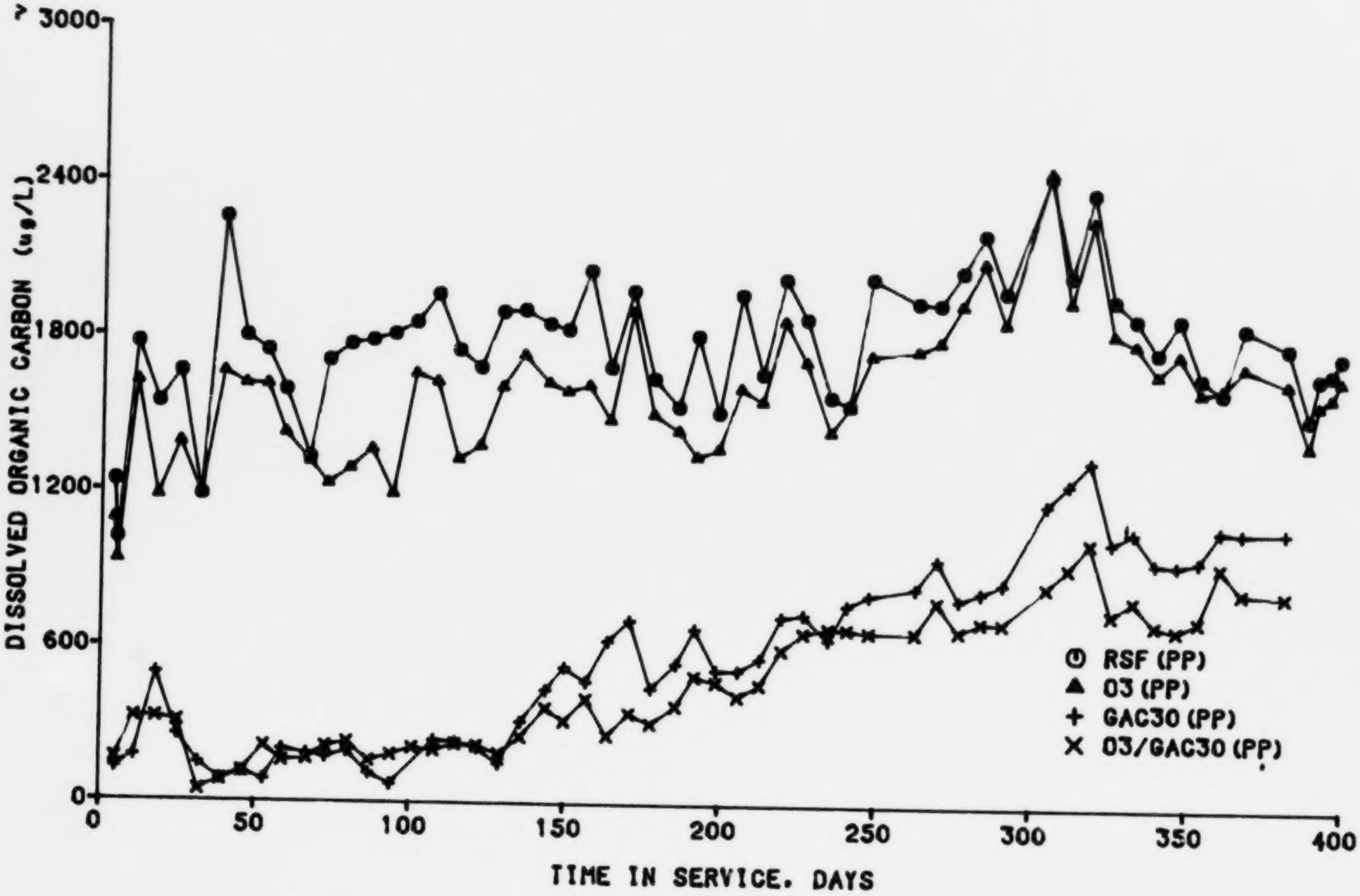

Figure 67. DOC levels through the Pilot Plant adsorption systems (30 min. EBCT).

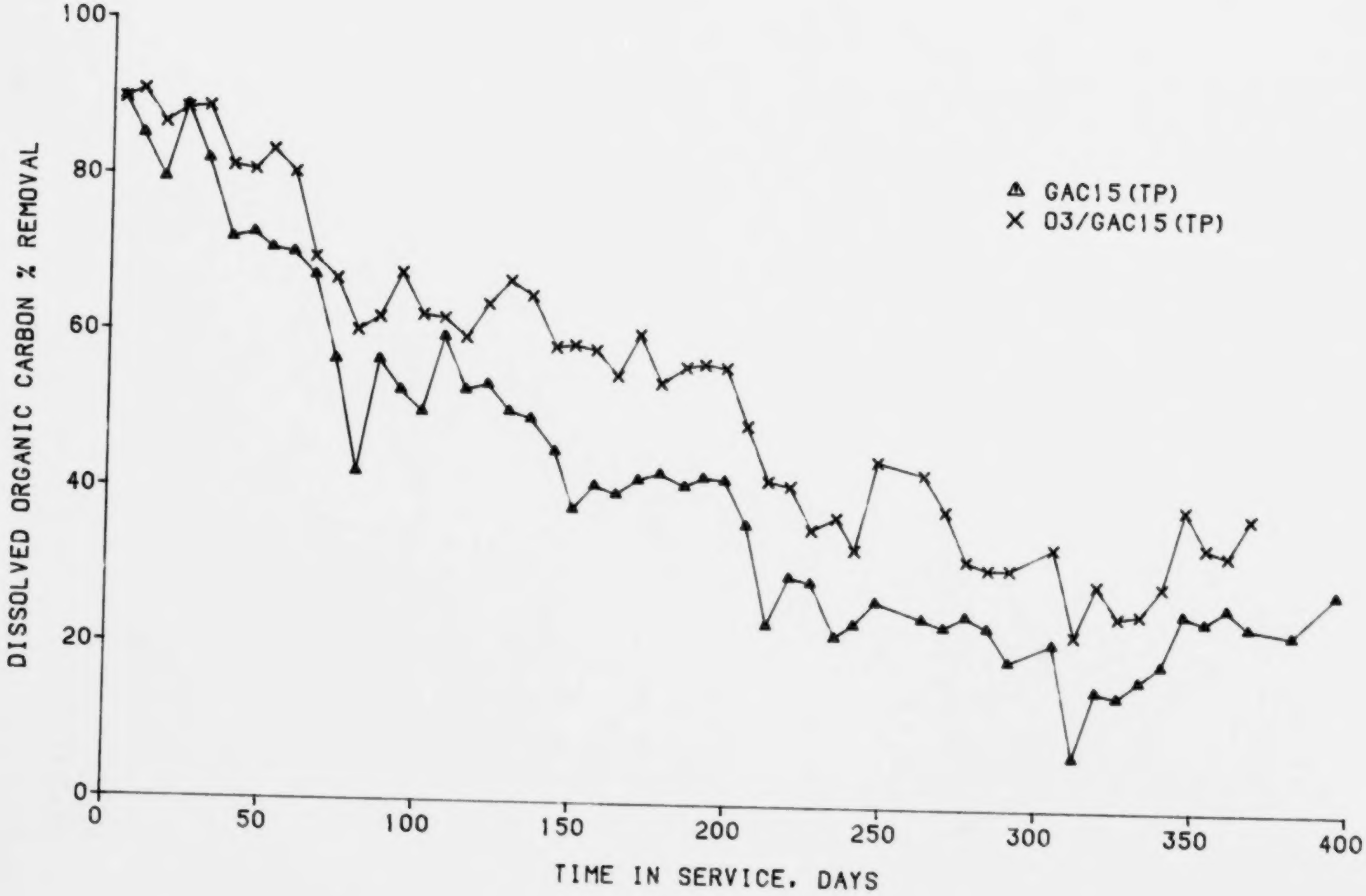

Figure 68. DOC removal through the Torresdale Plant adsorption systems (15 min. EBCT).

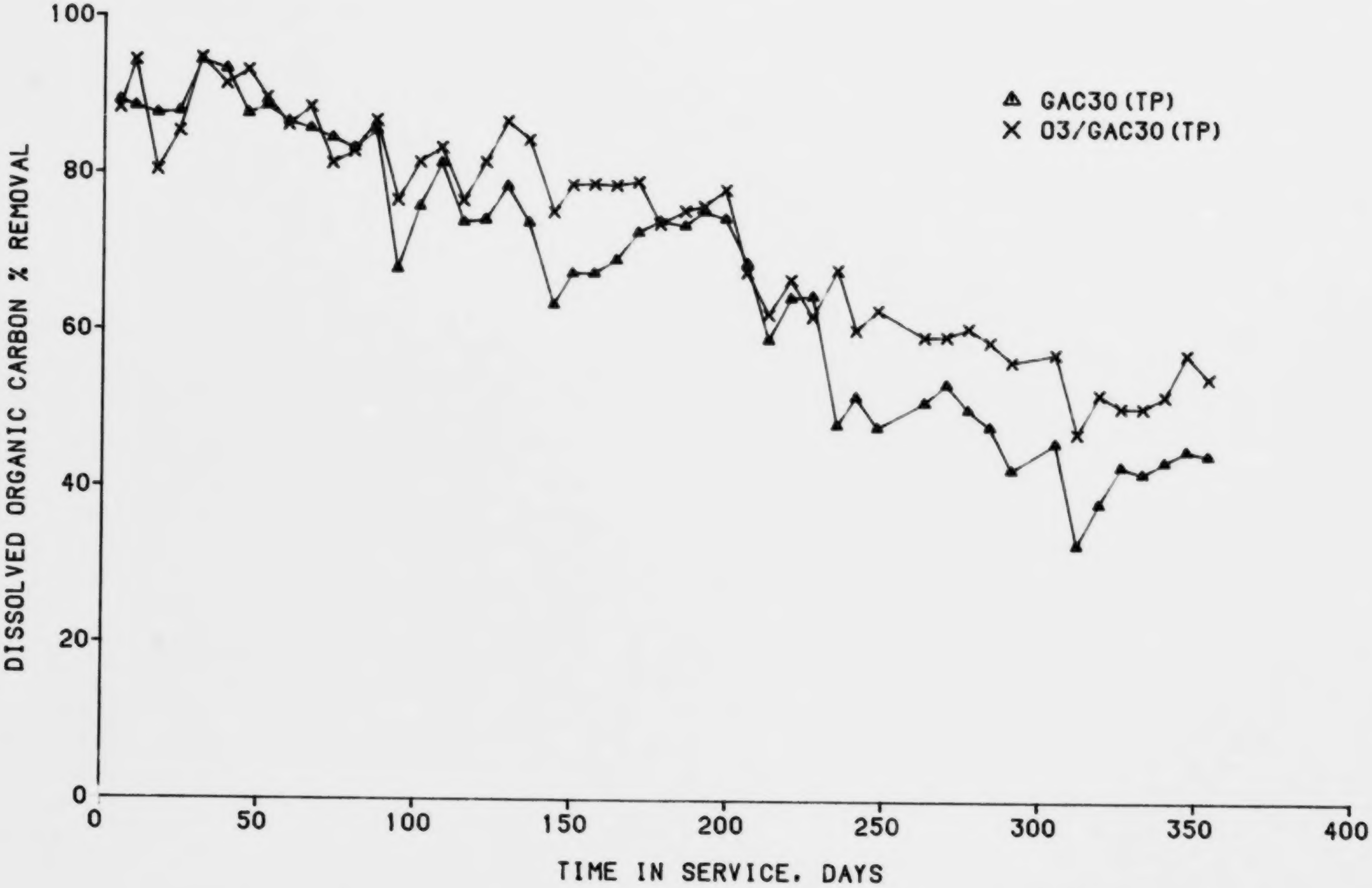

Figure 69. DOC removal through the Torresdale Plant adsorption systems (30 min. EBCT).

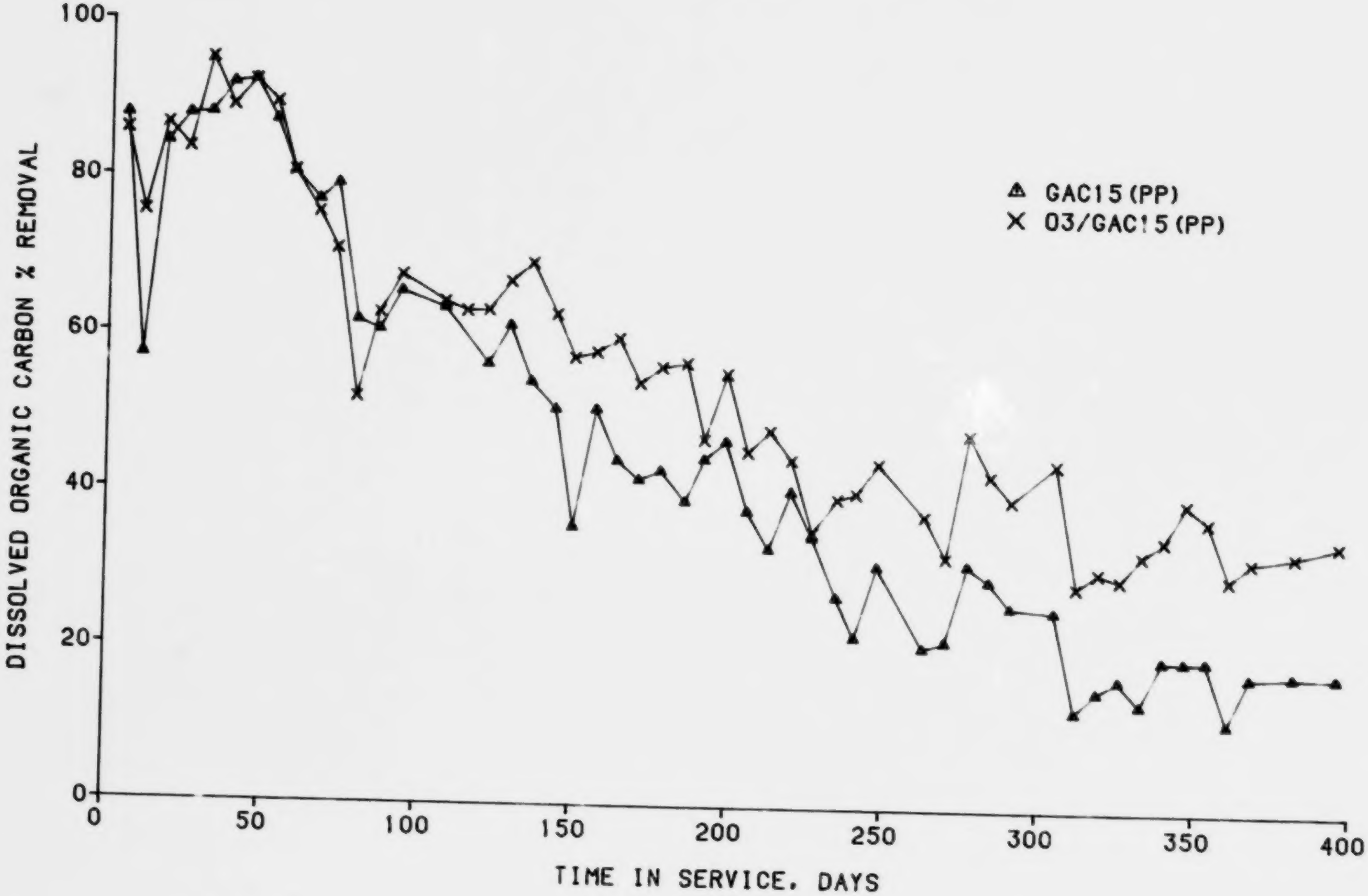

Figure 70. DOC removal through the Pilot Plant adsorption systems (15 min. EBCT).

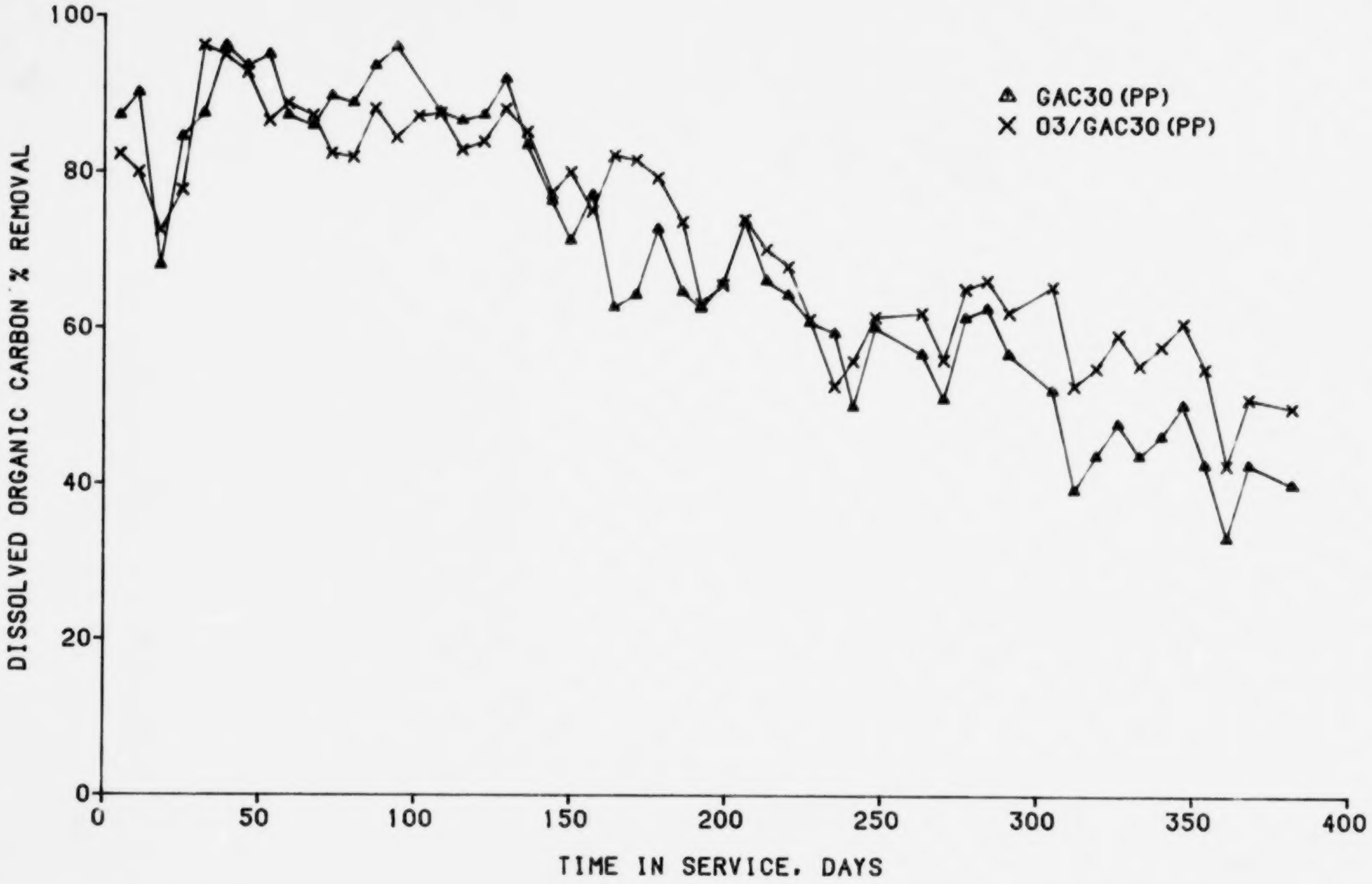

Figure 71. DOC removal through the Pilot Plant adsorption systems (30 min. EBCT).

TABLE 49. DAYS TO BREAKTHROUGH[1] (DOC = 400 ppb)

	GAC_{15}	GAC_{30}	O_3/GAC_{15}	O_3/GAC_{30}
Torresdale Plant	32	68	36	69
Pilot Plant	73	140	73	156

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[1] Based on 3-week running averages.

TABLE 50. CUMULATIVE DOC LOADING[1] AT BREAKTHROUGH (mg DOC/g GAC)

	GAC_{15}	GAC_{30}	O_3/GAC_{15}	O_3/GAC_{30}
Torresdale Plant	15	17	17	17
Pilot Plant	28	29	24	27

---

[1] Based on days to breakthrough (shown in Table 49).

DOC concentrations during conditions of steady-state removal are presented in Table 51. The averages shown are based on the data collected during the final three months of the first year of the study. During this time, percent removals through each of the 15 minute adsorption systems did not vary by more than ± 10% of the stated averages. Inspection of the DOC percent removal curves (Figures 65 to 68) will confirm that steady-state conditions had been achieved. In addition, Figures 72 and 73 present the concentration and percent removal curves, respectively, for the Pilot Plant GAC_{15} and O_3/GAC_{15} systems between days 200 to 600. These two systems, which remained in operation six months longer than the other adsorption systems, provide further evidence that steady-state conditions prevailed during this time.

During steady-state conditions, preozonation had a significant effect on DOC levels. For example, an additional 361 ppb DOC was removed through Torresdale Plant adsorption system with preozonation than through the GAC system alone. Of this additional removal, 93 ppb was due to direct DOC reductions in the ozone contactor. Similar values were obtained through the Pilot Plant system, where an additional 388 ppb DOC was removed by the GAC when preozonation was employed (with 85 ppb DOC loss due to oxidation in the

TABLE 51. STEADY-STATE REMOVAL OF DOC[1]

Torresdale Plant				Pilot Plant			
Site	Conc(ppb)	Δ(ppb)	%Δ	Site	Conc(ppb)	Δ(ppb)	%Δ
(5) RSF	2608			(14) RSF	2017		
(7) GAC_{15}	2113	495	19	(21) GAC_{15}	1618	399	20
(5) RSF	2608			(14) RSF	2017		
(6D) O_3RT	2515	93	4	(15D) O_3RT	1932	85	4
(6D) O_3RT	2515			(15D) O_3RT	1932		
(9) O_3/GAC_{15}	1752	763	30	(16) O_3/GAC_{15}	1230	702	36
				(15D) O_3RT	1932		
				(19) $O_3/SAND_{15}$	1688	244	13

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[1] Weighted Averages of samples collected from 1/14/81 to 4/14/81.

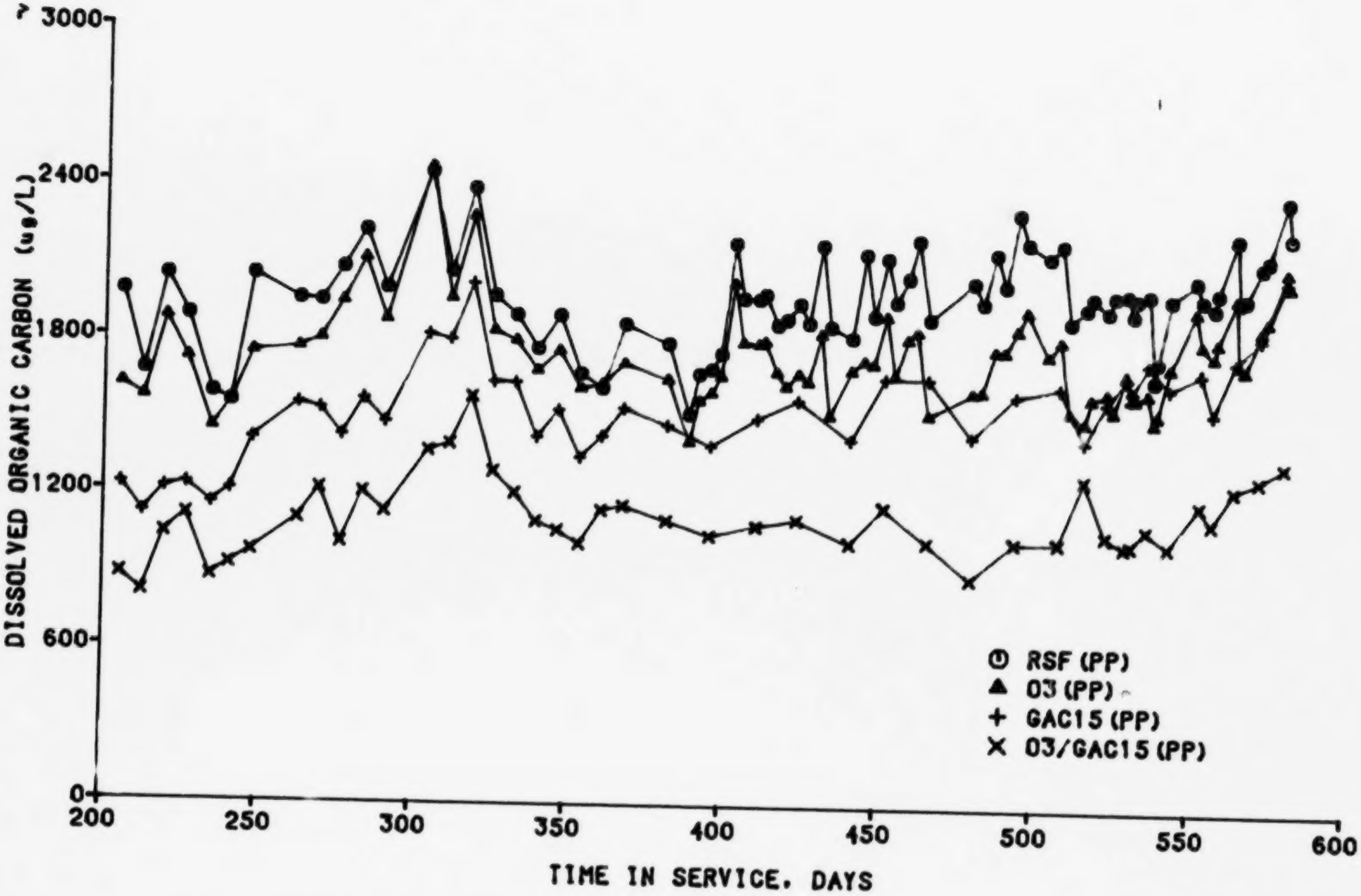

Figure 72. Steady state DOC levels through the Pilot Plant adsorption systems.

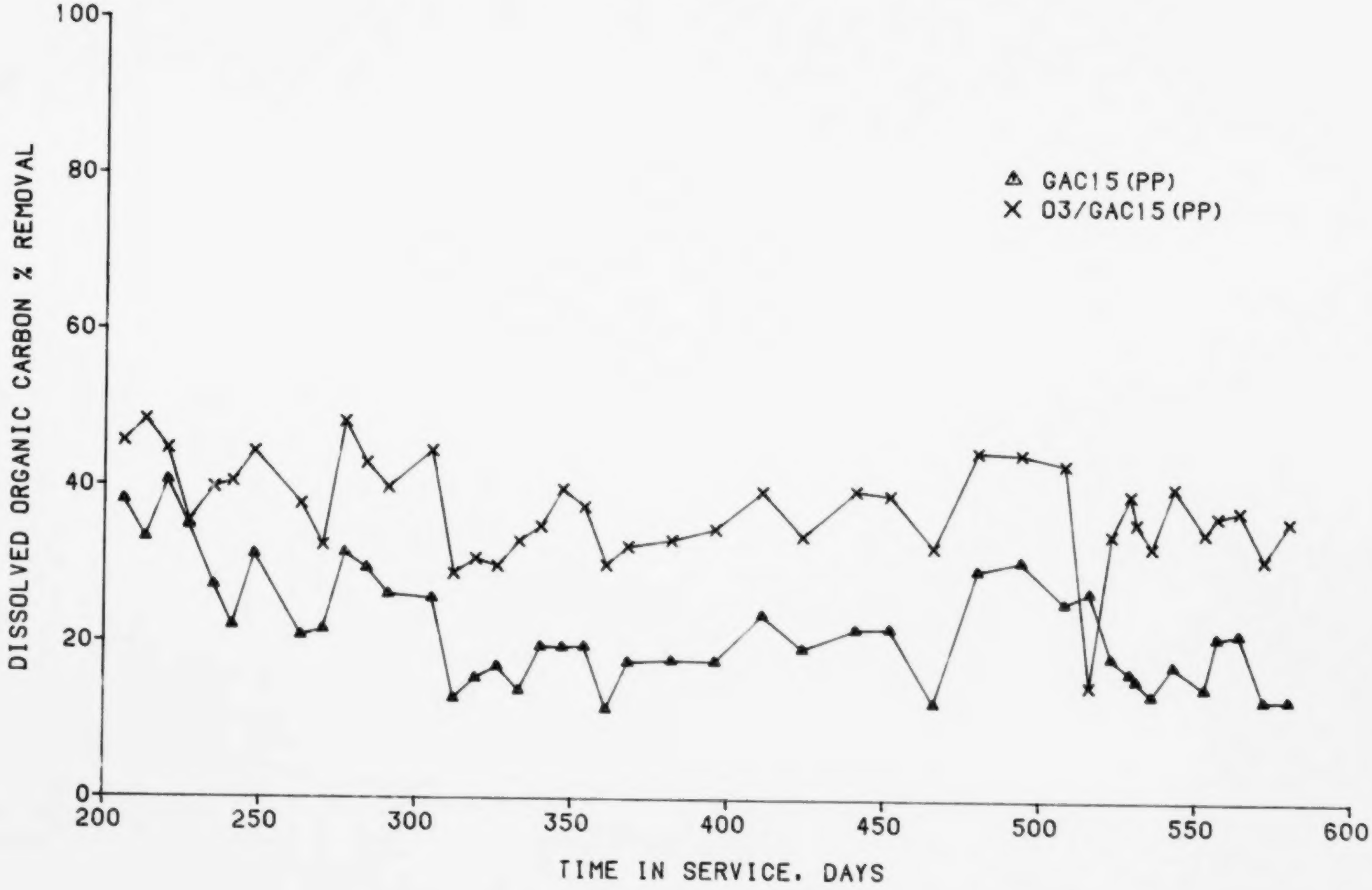

Figure 73. Steady state DOC removal through the Pilot Plant adsorption systems.

ozone contactor). During the same time period, 329 ppb DOC was removed through the O_3/$SAND_{15}$(PP) system. The proximity of these three values lends itself to the observation that an improvement of the GAC process through preozonation is, at least with respect to long-term removal capability, controlled by the same mechanism of removal that is evidenced on the O_3/$SAND_{15}$ system, i.e. biological degradation.

Table 52 lists the average DOC levels through the 15 minute EBCT adsorption systems. The averages are based on the data collected during the first year of study and thus include data from all three phases of breakthrough. In general, the Torresdale Plant systems removed more DOC than the comparable Pilot Plant systems. However, since the Torresdale Plant systems had higher organic loadings, the percent of DOC removal through the Torresdale Plant systems were lower than those observed through the Pilot Plant.

Trihalomethane Formation Potential (THMFP)--THMFP concentrations through the Torresdale and Pilot Plant adsorption systems are presented in Figures 74 to 77. The influent THMFP concentration to each adsorption system was seen to vary widely over time. An attempt to correlate THMFP influent levels with DOC resulted in R values ranging from -0.08 to +0.40. The adsorption system effluents displayed more uniformity; correlations for the 15 minute EBCT systems ranged from 0.74 to 0.83. Although the THMFP data exhibited much more scattering than was evident for the DOC data, the same general breakthrough pattern was observed for both. Another perspective of the THMFP results is offered in Figures 78 to 81, where percent removal curves are presented.

Average THMFP levels through the four adsorption systems during the first year of the study period are presented in Table 53. These results, like those for DOC, include data from all phases of breakthrough. Also like the DOC results, the Pilot Plant systems remove a greater percentage of the precursors than the comparable Torresdale Plant systems, as does preozonation. It is interesting to note that although the THMFP levels were increased through the Torresdale ozone contactor, the O_3/GAC_{15}(TP) system maintained lower effluent precursor levels than the GAC_{15}(TP) system, again indicating the effect of increased biodegradability.

Table 54 presents the steady-state removal levels for THMFP. Steady-state removal is also demonstrated in Figures 82 and 83 which show concentration and percent removal curves, respectively, for the GAC_{15} (PP) and the O_3/GAC_{15}(PP) systems. During steady-state conditions, prechlorination appeared to have only a minimal influence on THMFP removal. Preozonation, however, did appear to have a significant effect.

Specific Organics--The effectiveness of the four adsorption systems for the removal of the most prevalent specific organic compounds monitored by the purge and trap method are presented. Removal curves and percent reduction plots are presented for the compounds found to be consistently greater than 0.1 ppb. The compounds in this group include the trihalomethanes (chloroform, dichlorobromomethane and dibromochloromethane), 1,2-dichloropropane and acetone. Due to their lower concentration and less frequent detection, the quantitative results for the breakthrough of specific organic compounds

TABLE 52. AVERAGE DOC LEVELS[1]

Torresdale Plant				Pilot Plant			
Site	Conc(ppb)	Δ(ppb)	%Δ	Site	Conc(ppb)	Δ(ppb)	%Δ
(5) RSF	2559			(14) RSF	1826		
(7) GAC_{15}	1523	1036	40.5	(21) GAC_{15}	1008	818	44.8
(5) RSF	2559			(14) RSF	1826		
(6D) O_3RT	2452	107	4.2	(15D) O_3RT	1622	204	11.2
(6D) O_3RT	2452			(15D) O_3RT	1622		
(9) O_3/GAC_{15}	1173	1279	52.2	(16) O_3/GAC_{15}	750	872	53.8
				(15D) O_3RT	1622		
				(19) $O_3/SAND_{15}$	1395	227	14.0

[1] Weighted Averages of samples collected from 4/14/80 to 4/14/81.

TABLE 53. AVERAGE THMFP LEVELS[1]

Torresdale Plant				Pilot Plant			
Site	Conc(ppb)	Δ(ppb)	%Δ	Site	Conc(ppb)	Δ(ppb)	%Δ
(5) RSF	99			(14) RSF	119		
(7) GAC_{15}	61	38	38.4	(21) GAC_{15}	57	62	52.1
(5) RSF	99			(14) RSF	119		
(6D) O_3RT	105	-6	-6.0	(15D) O_3RT	100	19	15.9
(6D) O_3RT	105			(15D) O_3RT	100		
(9) O_3/GAC_{15}	48	57	54.3	(16) O_3/GAC_{15}	39	61	61.0
				(15D) O_3RT	100		
				(19) $O_3/SAND_{15}$	86	14	14.0

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[1] Weighted Averages of samples collected from 4/14/80 to 4/14/81.

TABLE 54. STEADY-STATE REMOVAL OF THMFP[1]

Torresdale Plant				Pilot Plant			
Site	Conc(ppb)	Δ(ppb)	%Δ	Site	Conc(ppb)	Δ(ppb)	%Δ
(5) RSF	116			(14) RSF	111		
(7) GAC_{15}	91	25	21.6	(21) GAC_{15}	84	27	24.3
(5) RSF	116			(14) RSF	111		
(6D) O_3RT	124	-8	-6.9	(15D) O_3RT	91	20	18.0
(6D) O_3RT	124			(15D) O_3RT	91		
(9) O_3/GAC_{15}	83	41	33.1	(16) O_3/GAC_{15}	56	35	38.5
				(15D) O_3RT	91		
				(19) $O_3/SAND_{15}$	77	14	15.4

[1] Weighted averages of samples collected from 1/14/81 to 4/14/81.

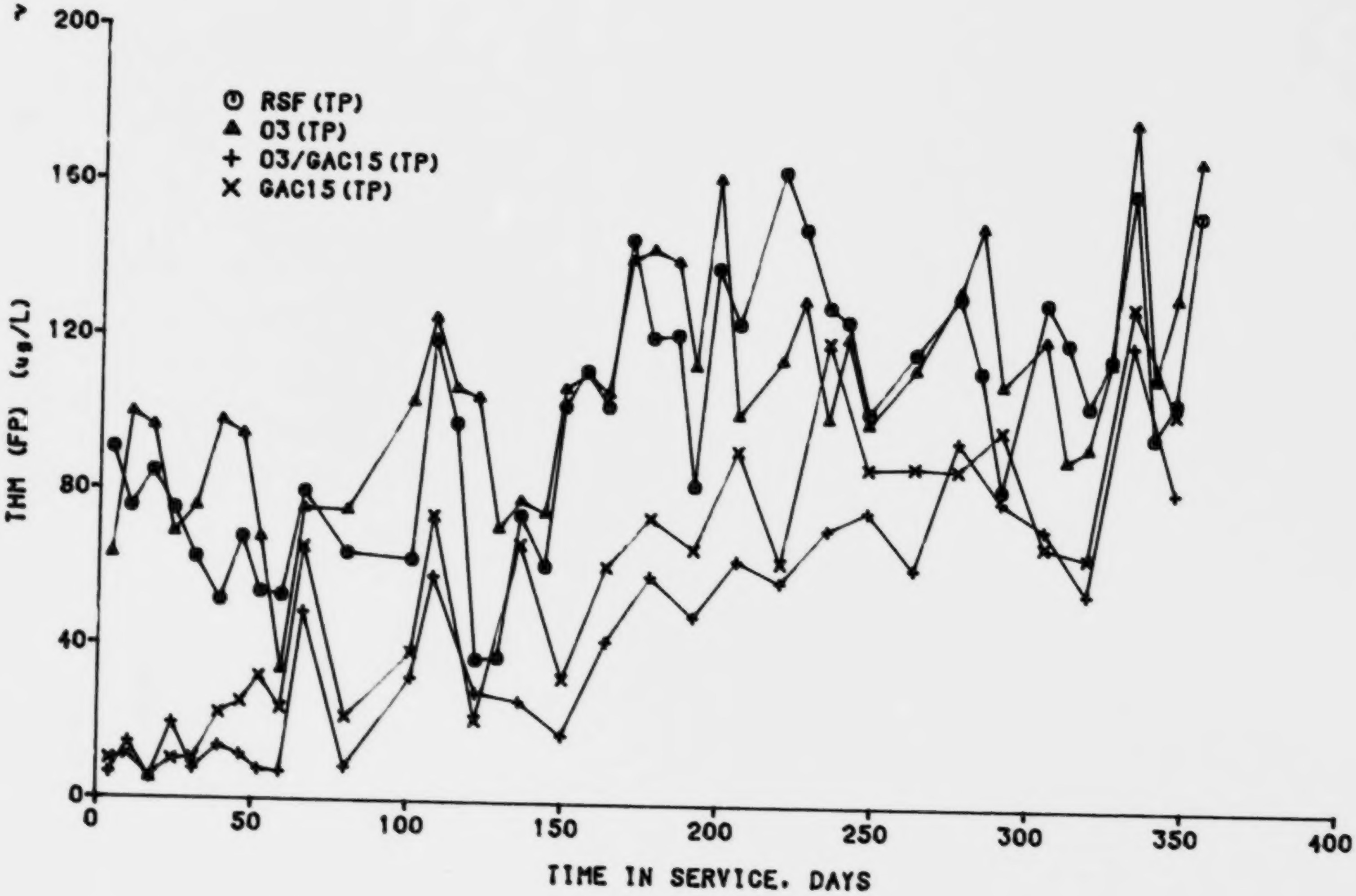

Figure 74. THMFP levels through the Torresdale Plant adsorption systems (15 min. EBCT).

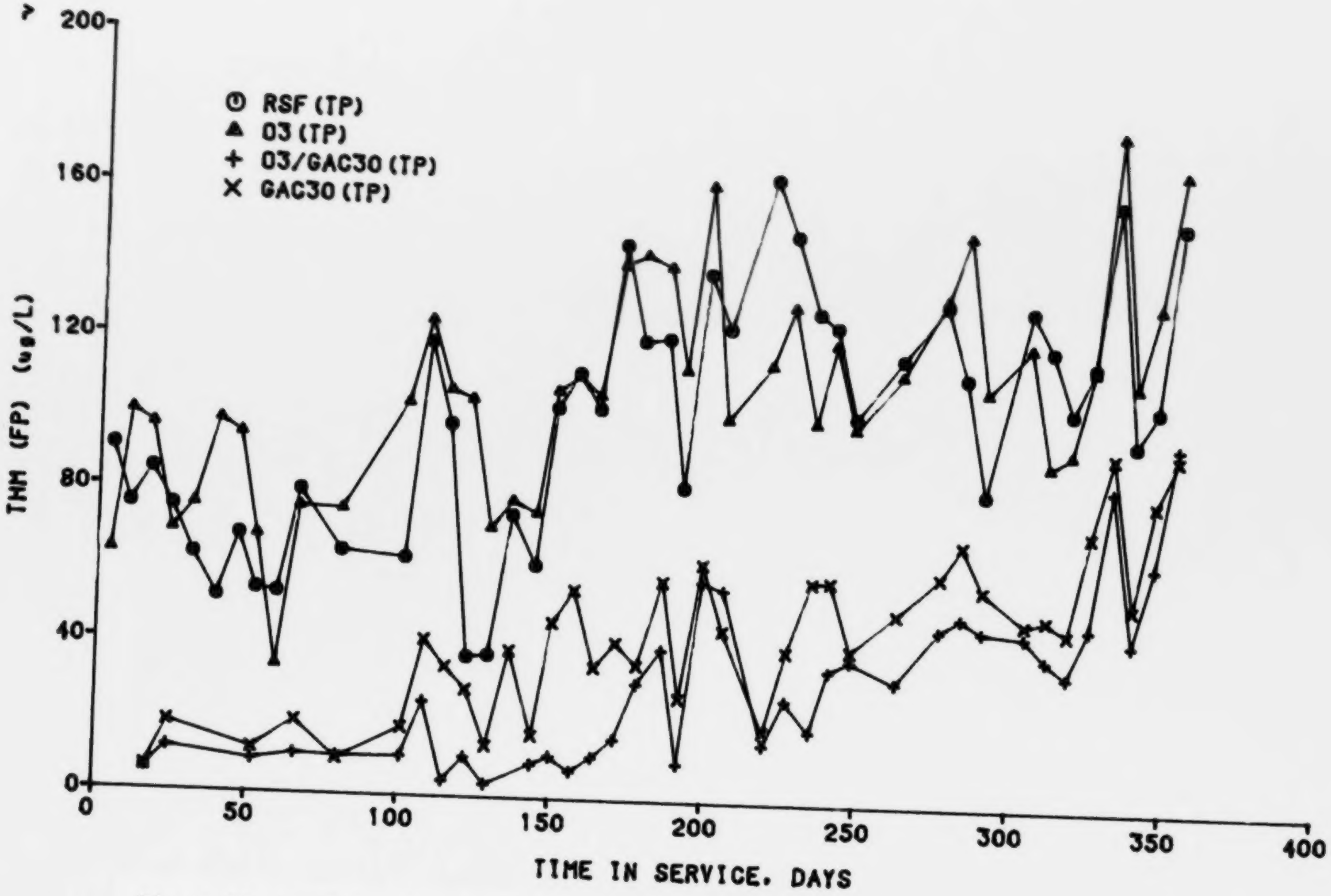

Figure 75. THMFP levels through the Torresdale Plant adsorption systems (30 min. EBCT).

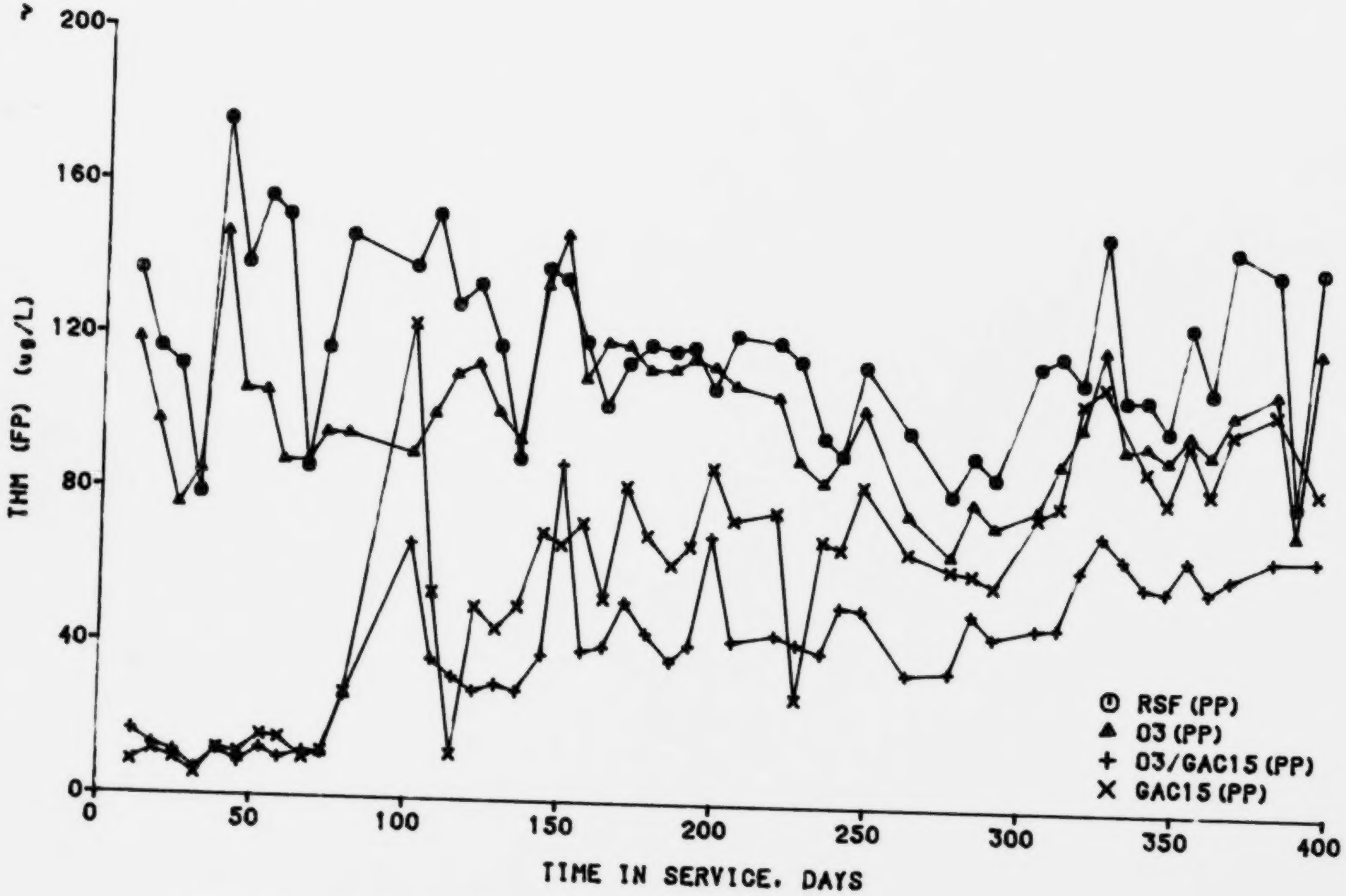

Figure 76. THMFP levels through the Pilot Plant adsorption systems (15 min. EBCT).

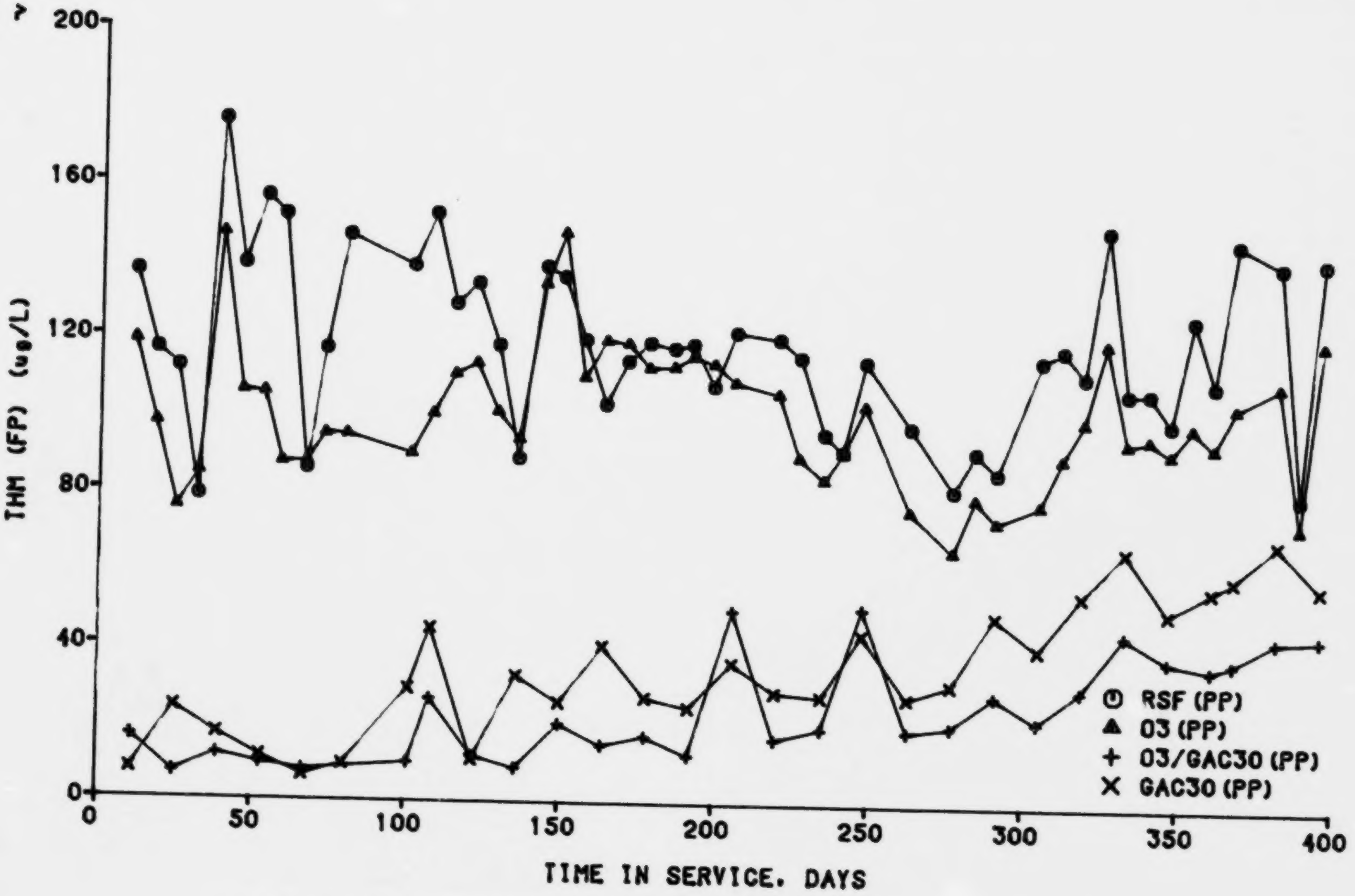

Figure 77. THMFP levels through the Pilot Plant adsorption systems (30 min. EBCT).

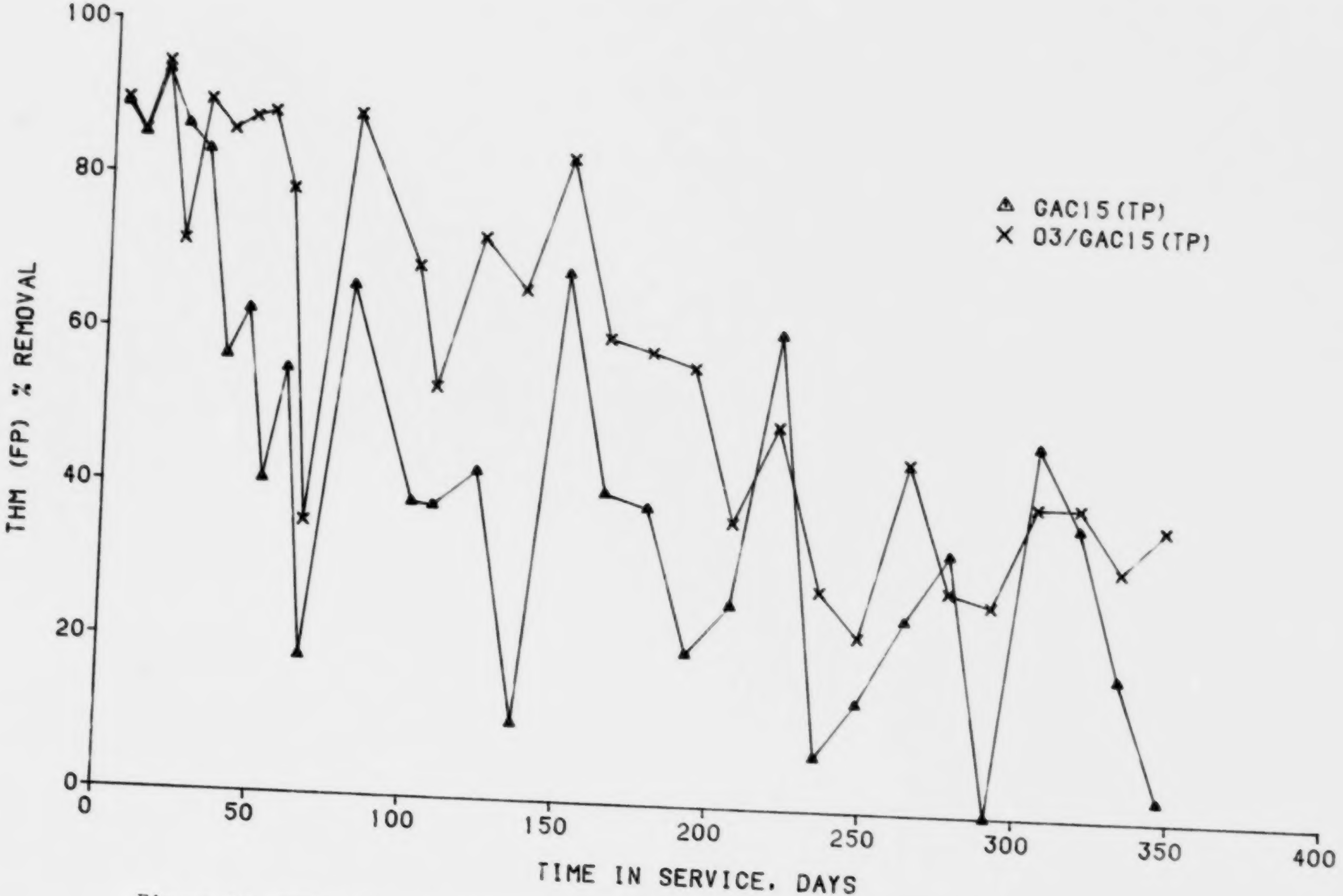

Figure 78. THMFP removal through the Torresdale Plant adsorption systems (15 min. EBCT).

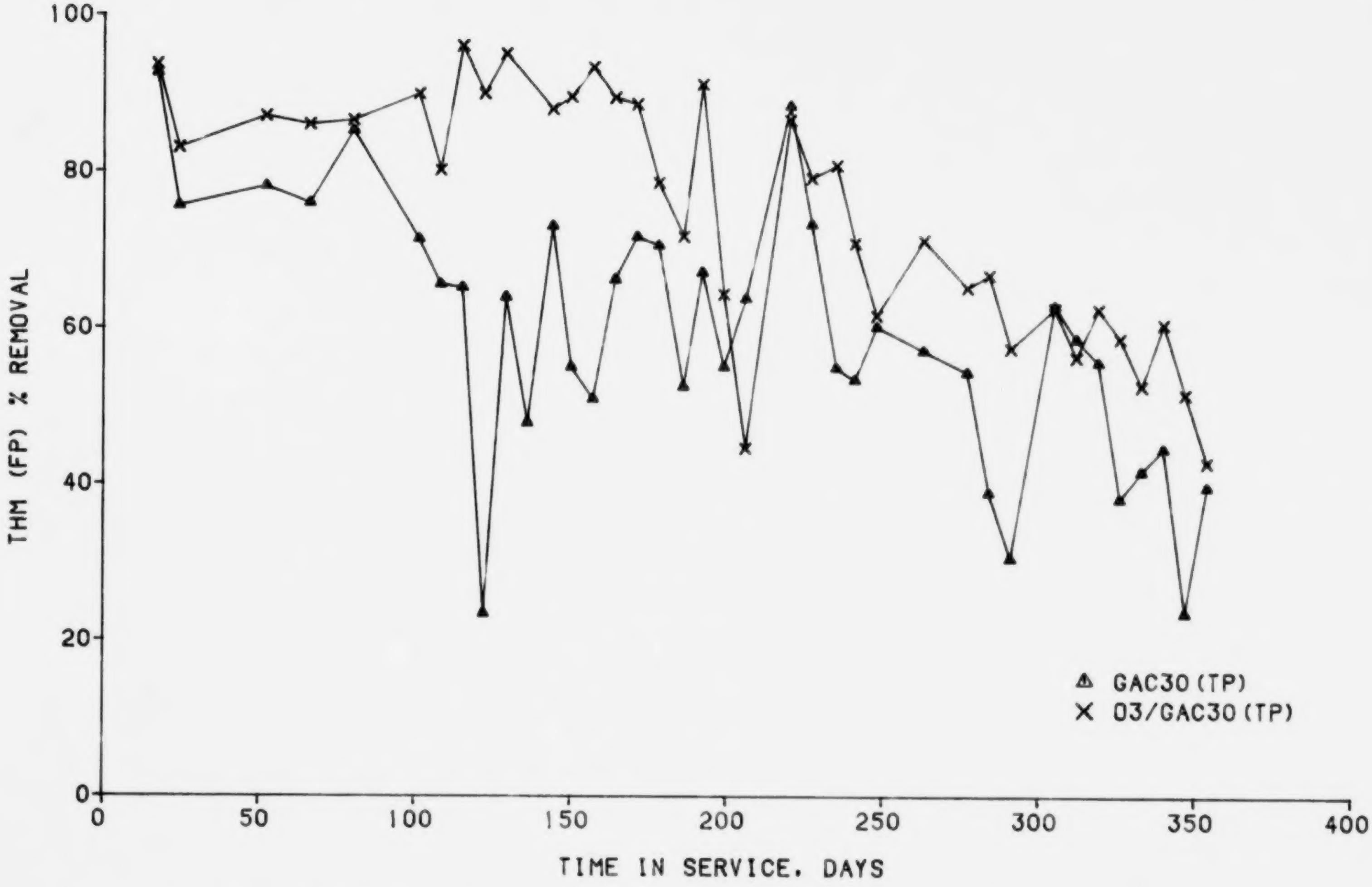

Figure 79. THMFP removal through the Torresdale Plant adsorption systems (30 min. EBCT).

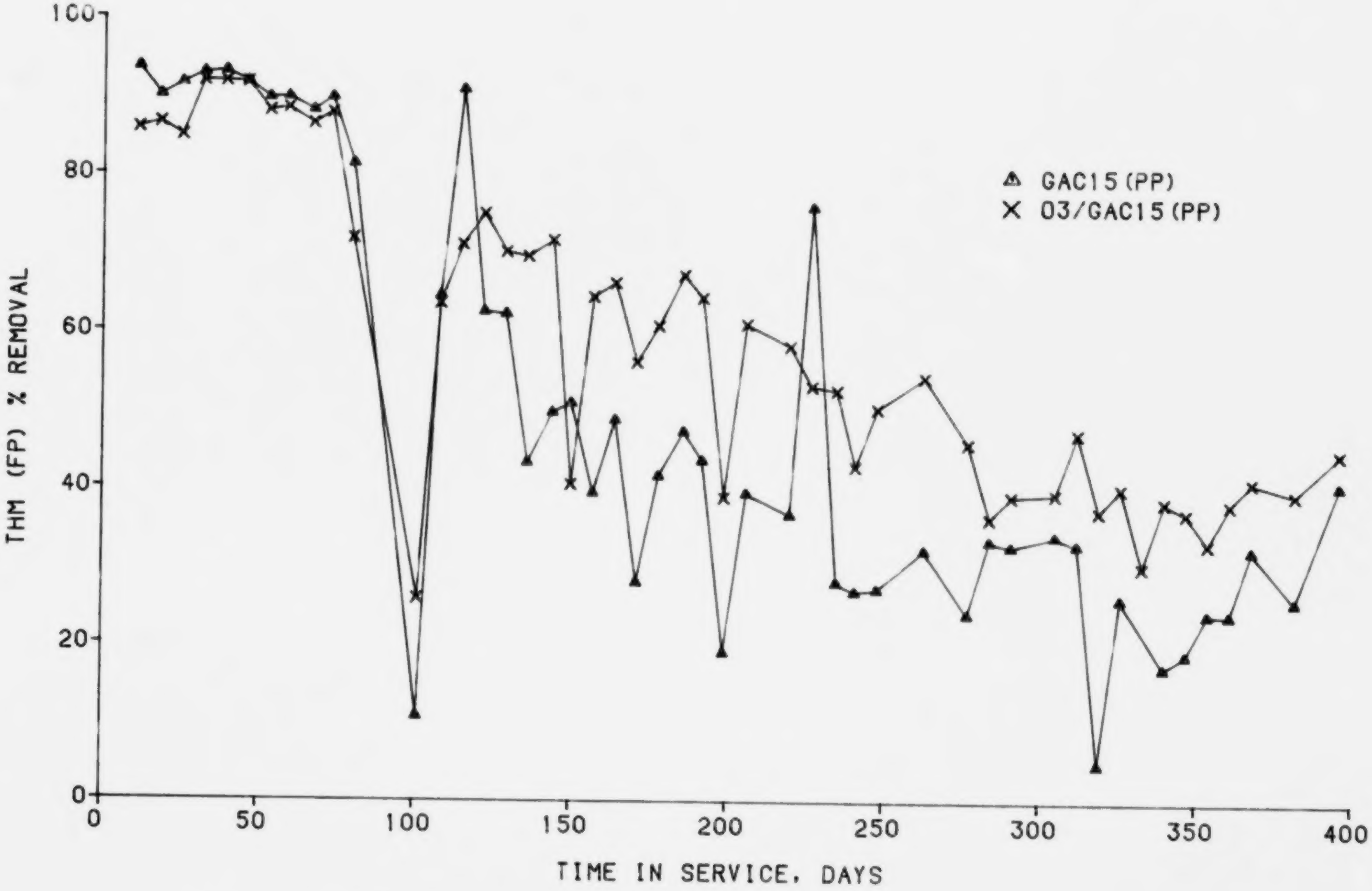

Figure 80. THMFP removal through the Pilot Plant adsorption systems (15 min. EBCT).

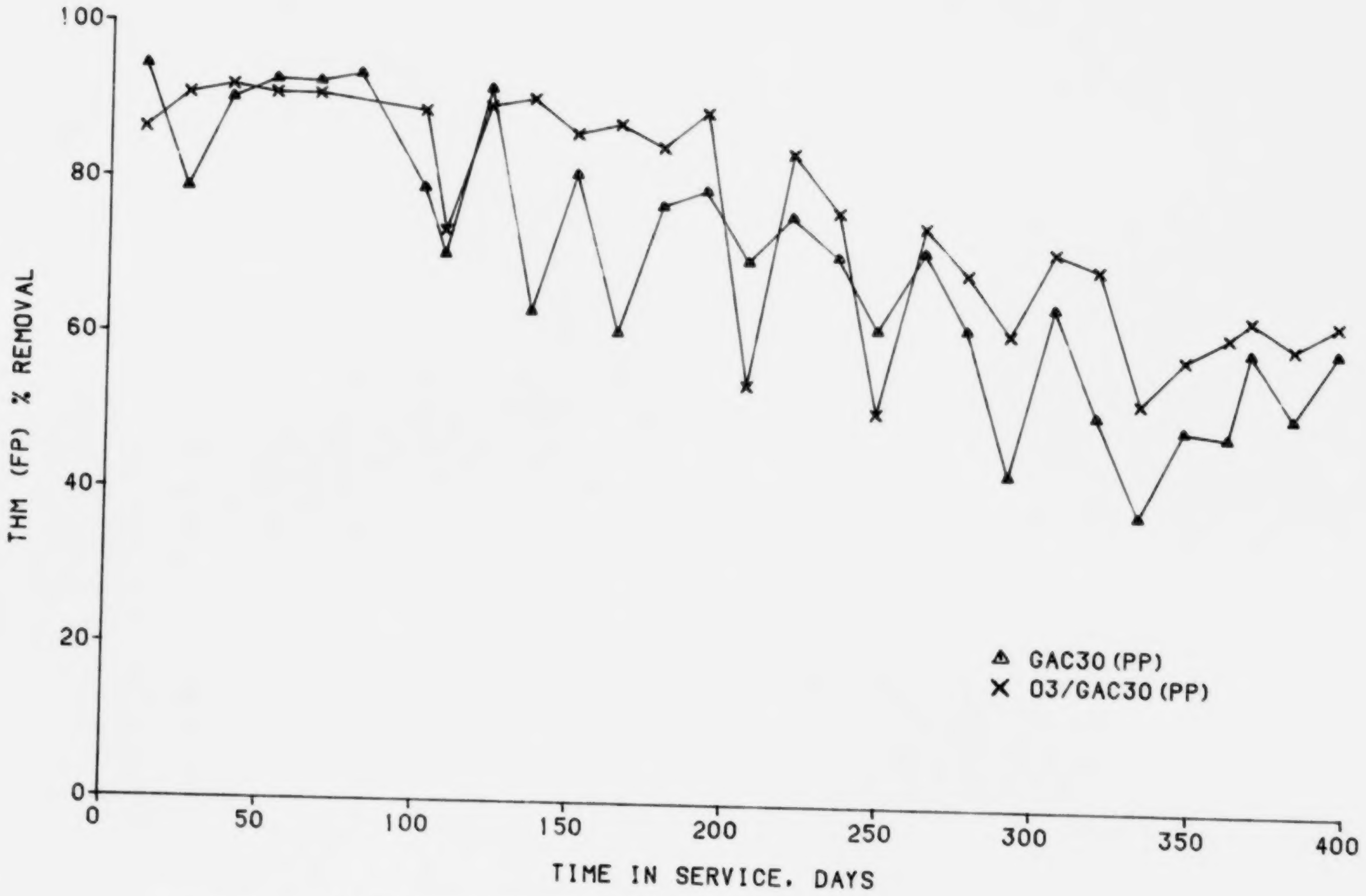

Figure 81. THMFP removal through the Pilot Plant adsorption systems (30 min. EBCT).

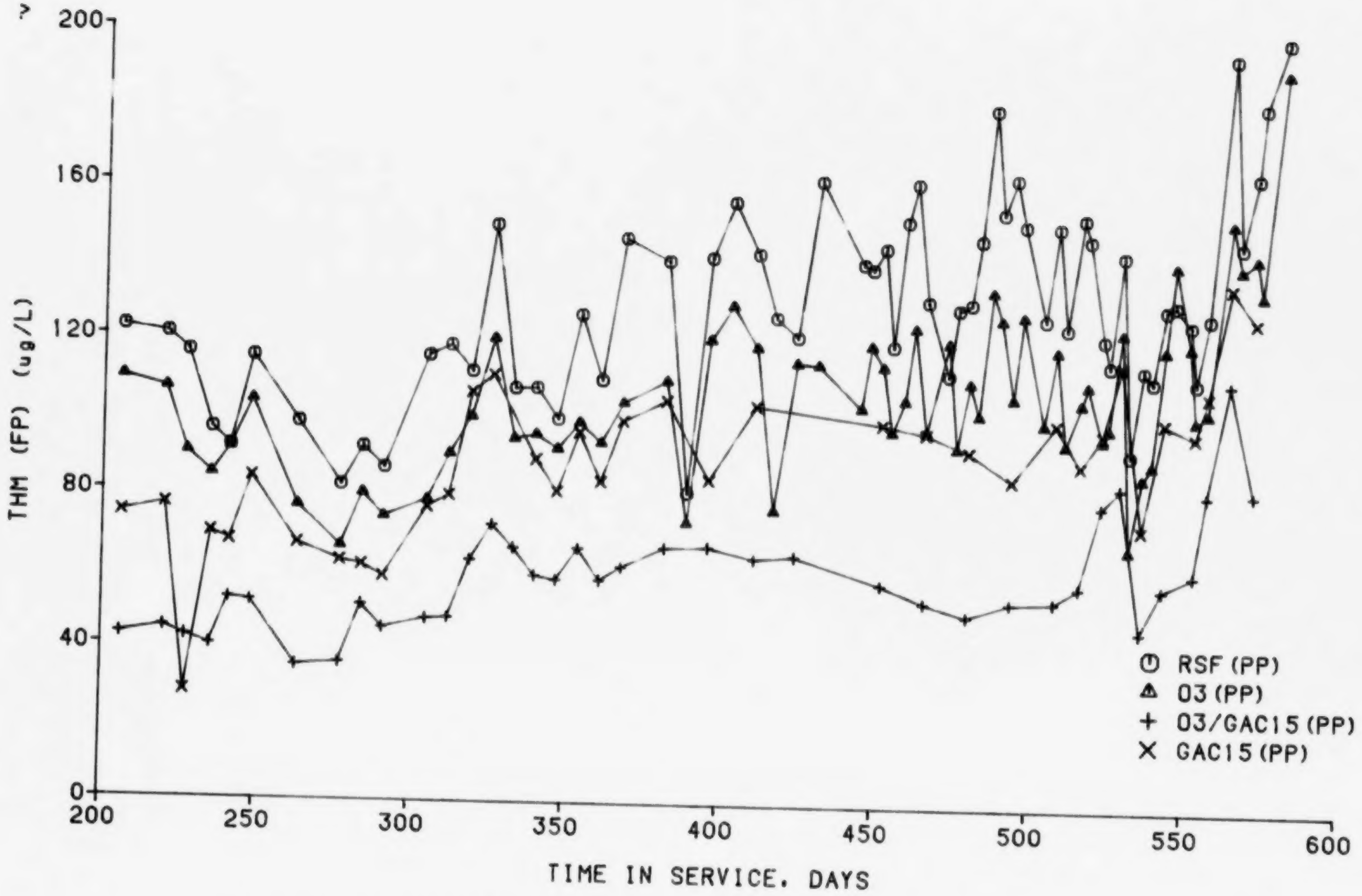

Figure 82. Steady state THMFP levels in the Pilot Plant adsorption systems.

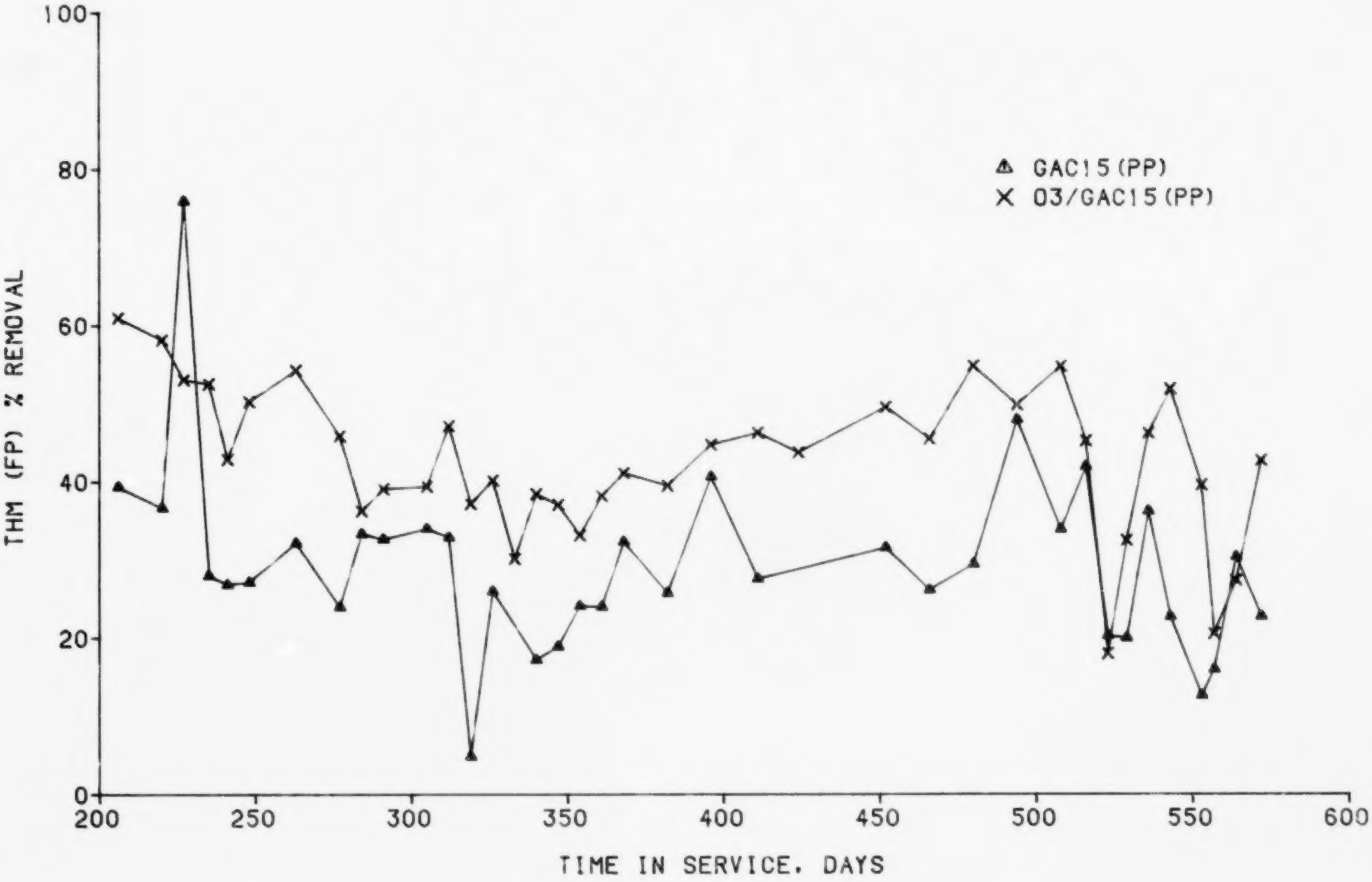

Figure 83. Steady state THMFP removal through the Pilot Plant adsorption systems.

measured by the purge and trap method are listed, but not plotted.

Chloroform levels through the Torresdale Plant GAC and O_3/GAC systems are presented in Figures 84 and 85. As expected, the 15 minute EBCT systems breakthrough nearly twice as quickly as the 30 minute systems (36). Unexpectedly, however, the O_3/GAC systems did not appear to have significantly longer times to breakthrough than their respective GAC systems. This may be seen more clearly in Figures 86 and 87, which show comparisons of percent removals (-100% to 100%) for the GAC (TP) and O_3/GAC (TP) systems. Significant sloughing of chloroform is observed after the initial adsorption period.

Dichlorobromomethane (DCBM) and dibromochloromethane (DBCM) breakthrough curves for the Torresdale systems are shown in the same format used for chloroform in Figures 88 to 95. Significant sloughing was also observed for DCBM after the initial adsorption period. No trihalomethane results from the Pilot Plant systems are presented here due to the generally low levels found in the Pilot Plant process waters (Table 42).

Figures 96 to 99 show the 1,2 dichloropropane (DCP) levels through the Torresdale Plant adsorption systems. Unlike the THMs, which were primarily produced only in the Torresdale Plant, DCP is a river contaminant which was of sufficient levels through the Pilot Plant system to plot the results. The results for the GAC(PP) and O_3/GAC(PP) systems are presented in Figures 100 and 101, respectively.

Figures 102 to 103 present the acetone results. Again, acetone is of special interest because it is a confirmed by-product of the ozonation process. It appears that acetone is continuously maintained at low effluent levels (i.e. below 5 ppb) no matter what the influent concentrations are. This is true for the GAC_{15} and the O_3/GAC_{15} systems of both the Torresdale and Pilot Plants. Acetone samples were not collected from the 30 minute EBCT systems.

Tables 55 and 56 show the influent and effluent concentrations from the Torresdale and Pilot Plant adsorption systems. In general, the Torresdale Plant systems breakthrough earlier than the comparable Pilot Plant systems. The order of breakthrough for the non-THM volatile organics is similar for both the GAC and the O_3/GAC systems of the Torresdale and Pilot Plants:

Acetone, Benzene, Methylene Chloride

Dimethoxymethane

1,2-Dichloropropane

1,2-Dichloroethane

1,1,1-Trichloroethane

1,1,2,2-Tetrachloroethylene

Carbon Tetrachloride

Trichloroethylene

Increasing Time To Breakthrough ↓

TABLE 55: GAC BREAKTHROUGH OF VOLATILE ORGANICS, TORRESDALE PLANT

COMPOUND	AVERAGE APPLIED[a]		WEEKS TO BREAKTHROUGH[b]	
	GAC_{15}	O_3/GAC_{15}	GAC_{15}	O_3/GAC_{15}
Total Trihalomethanes	99(207)	66(145)	immediate	immediate
Chloroform	73(163)	46(110)	immediate	immediate
Dichlorobromomethane	21(41)	15(28)	2	6
Dibromochloromethane	5.5(14)	4.8(9.6)	9	10
Bromoform	0.3(1.0)	0.3(0.9)	33	33
Acetone	14.2(72)	21(100)	immediate	immediate
Benzene	0.2(0.8)	0.2(0.7)	immediate	immediate
Methylene Chloride[c]	0.3(1.3)	0.3(1.1)	immediate	immediate
Dimethoxymethane	3.7(17)	3.1(14)	3	3
1,2-Dichloropropane	6.1(24)	4.8(22)	9	13
1,2-Dichloroethane	1.4(15)	1.3(14)	13	9
1,1,1-Trichloroethane	0.2(0.6)	0.1(0.5)	14	17
1,1,2,2-Tetrachloroethylene	0.4(1.6)	0.1(0.8)	17	17
Carbon Tetrachloride	1.0(16)	0.2(5.0)	21	never
Trichloroethylene	0.4(1.5)	0.4(1.3)	35	42

Detection Limit = 0.1 μg/l

[a] AVG(MAX)-concentrations in ug/l

[b] Weeks until >0.1ppb for >2 consistent weeks

[c] Possible laboratory contaminant level of 0.1 to 0.2 ppb

TABLE 56: GAC BREAKTHROUGH OF VOLATILE ORGANICS, PILOT PLANT

COMPOUND	AVERAGE APPLIED[a]		WEEKS TO BREAKTHROUGH[b]	
	GAC_{15}	O_3/GAC_{15}	GAC_{15}	O_3/GAC_{15}
Total Trihalomethanes	5.6(53)	3.8(33)	immediate	immediate
Chloroform	4.3(43)	2.8(26)	immediate	immediate
Dichlorobromomethane	1.0(11)	0.8(7.9)	2	immediate
Dibromochloromethane	0.3(2.7)	0.2(2.3)	25	27
Bromoform	<0.1(0.2)	<0.1(0.1)	never	never
Acetone	7.3(63)	9.4(67)	immediate	immediate
Benzene	0.2(0.7)	0.2(0.6)	immediate	immediate
Methylene Chloride[c]	0.3(1.8)	0.2(1.5)	immediate	immediate
Dimethoxymethane	4.1(19)	2.3(13)	<7	<6
1,2-Dichloropropane	4.5(19)	3.0(16)	17	14
1,2-Dichloroethane	1.2(9.0)	1.0(7.3)	14	14
1,1,1-Trichloroethane	0.2(0.8)	0.1(0.4)	19	34
1,1,2,2-Tetrachloroethylene	0.4(3.0)	0.1(0.9)	never	never
Carbon Tetrachloride	<0.1(0.6)	<0.1(0.2)	never	never
Trichloroethylene	0.2(0.7)	0.1(0.4)	37	never

Detection Limit = 0.1 ug/1

[a] AVG(MAX)-concentrations in ug/1

[b] Weeks until >0.1ppb for >2 consistent weeks

[c] Possible laboratory contaminant level of 0.1 to 0.2 ppb

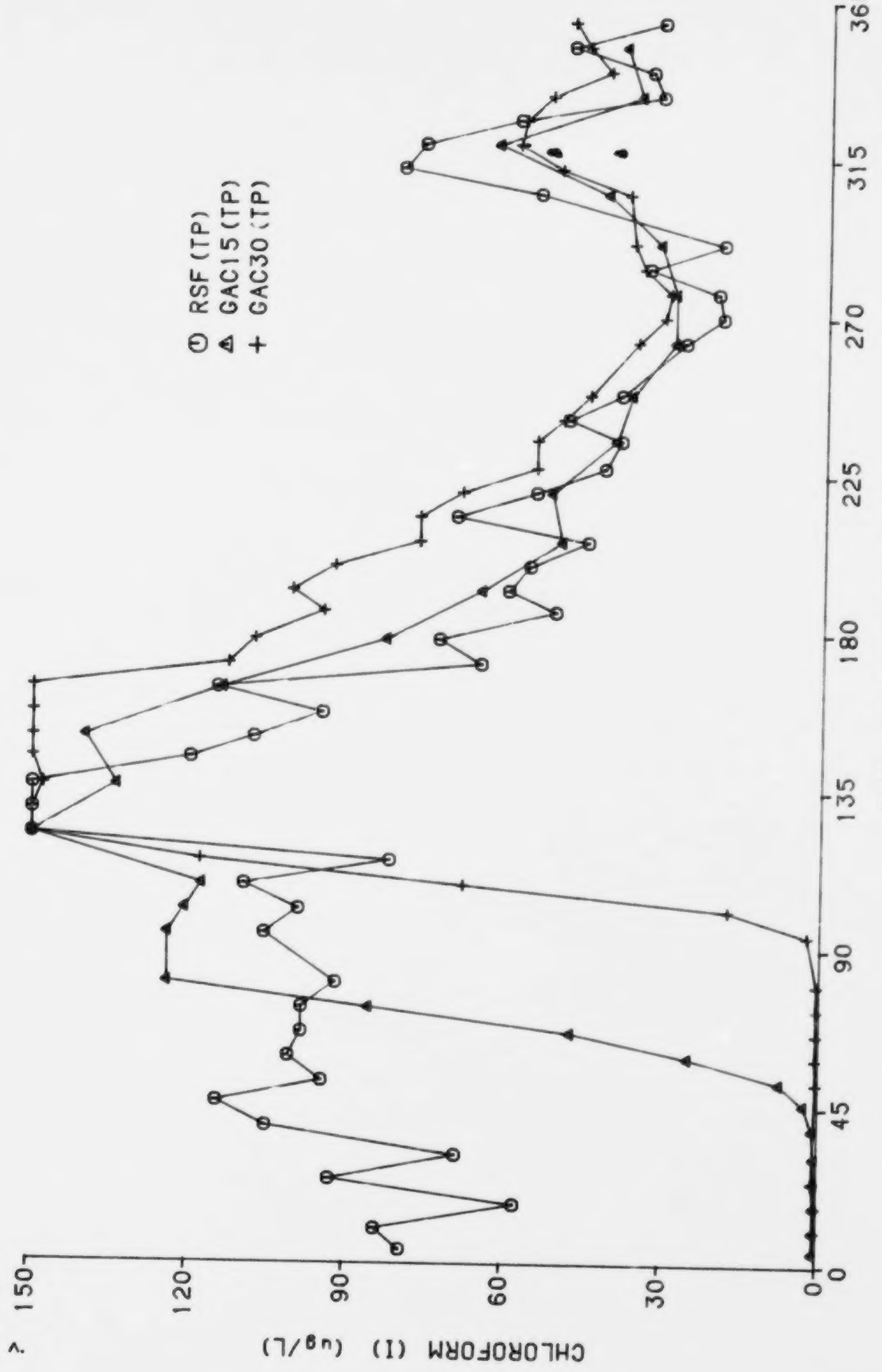

Figure 84. Chloroform levels through the Torresdale Plant GAC systems.

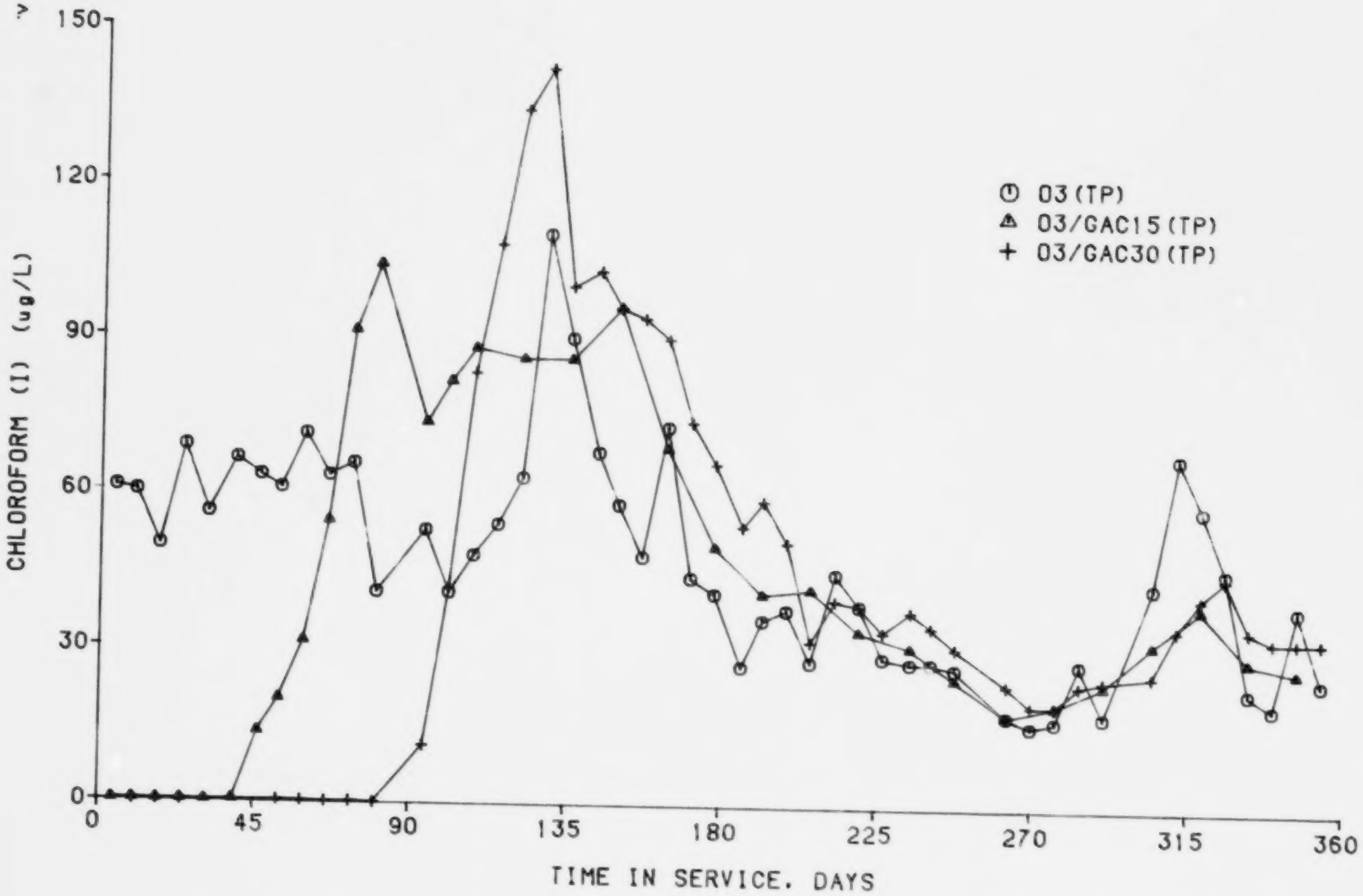

Figure 85. Chloroform levels through the Torresdale Plant O_3/GAC systems.

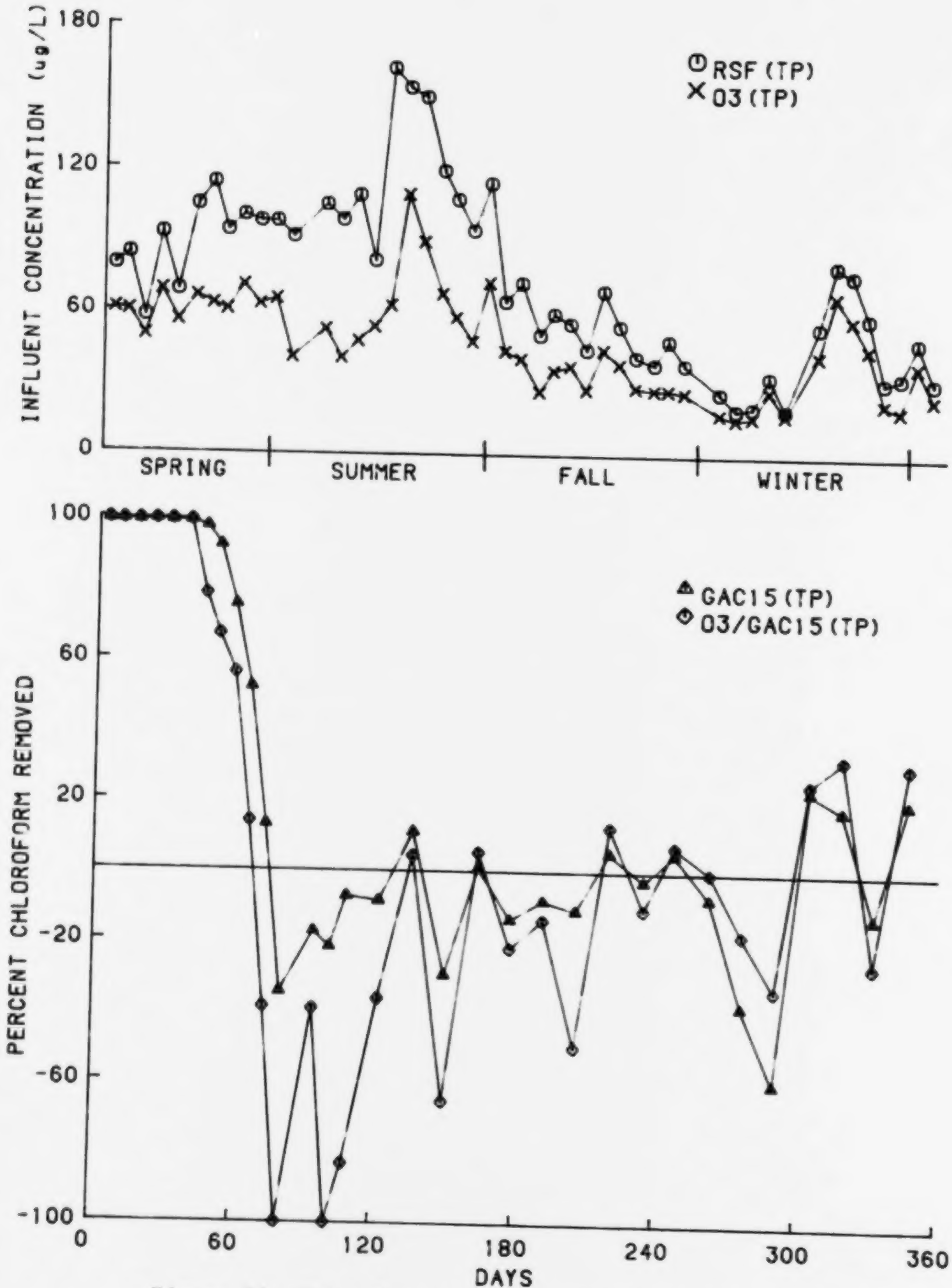

Figure 86. Chloroform removal through the Torresdale Plant adsorption systems (15 min. EBCT).

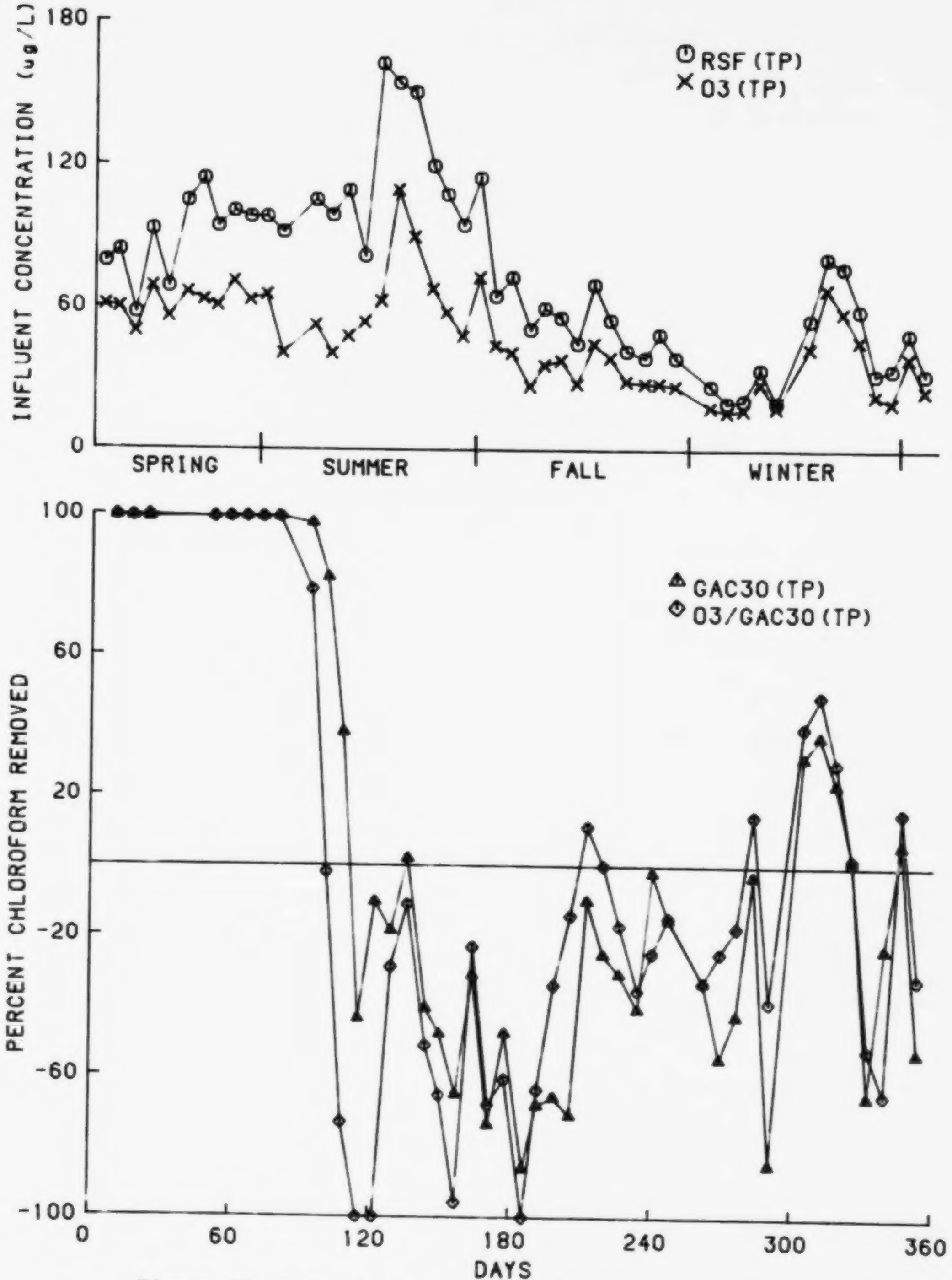

Figure 87. Chloroform removal through the Torresdale Plant adsorption systems (30 min. EBCT).

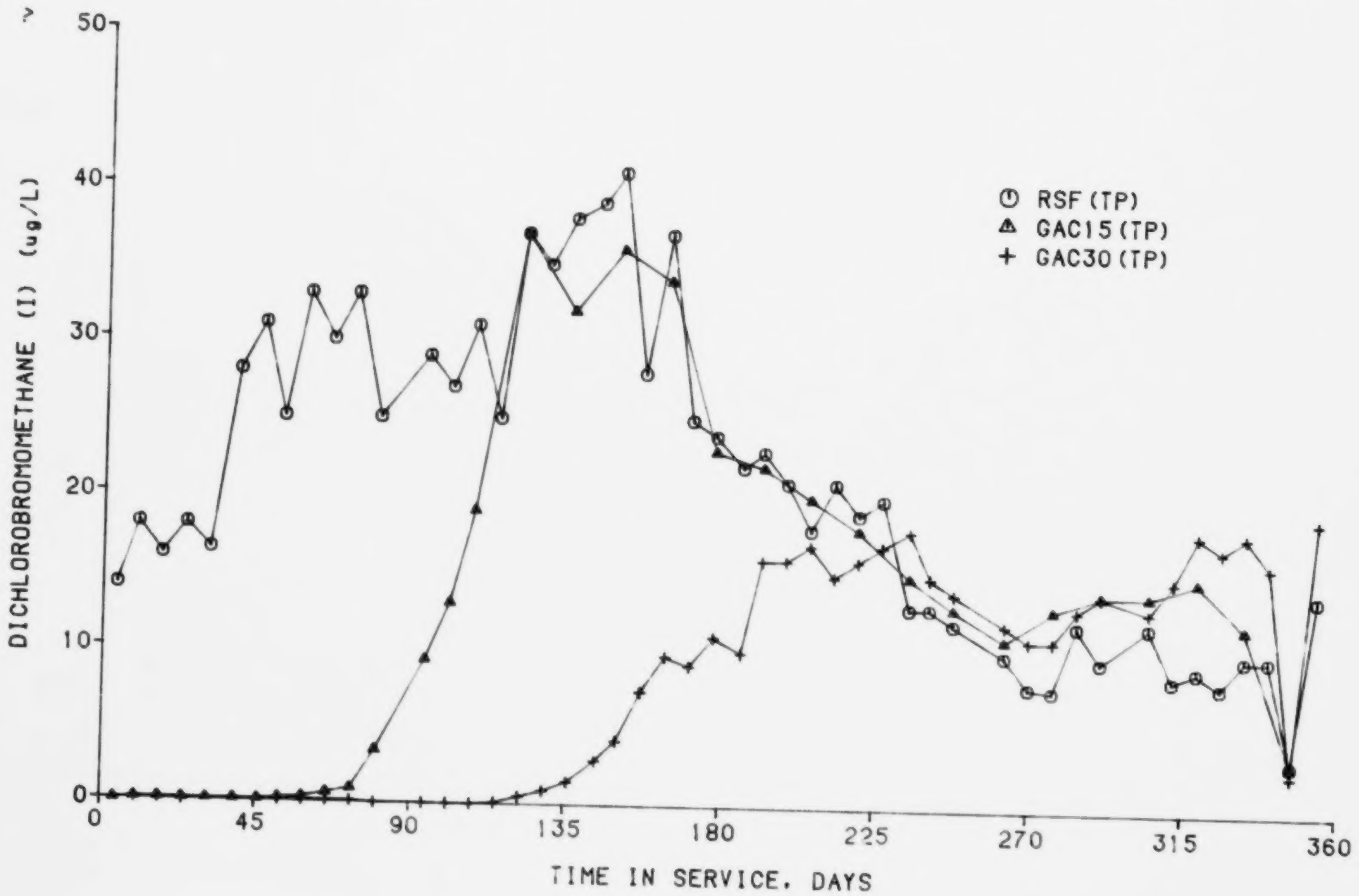

Figure 88. Dichlorobromomethane levels through the Torresdale Plant GAC systems.

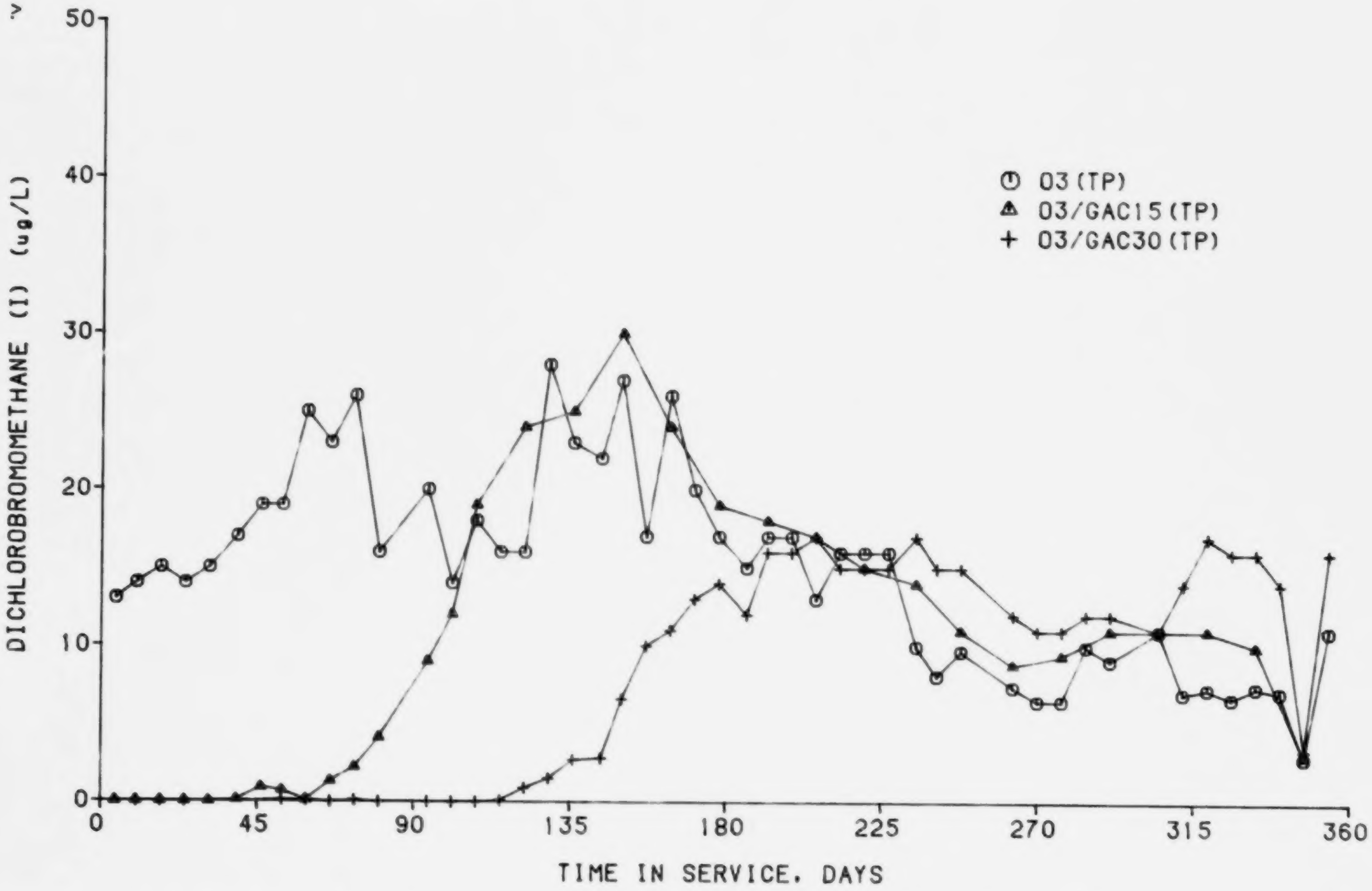

Figure 89. Dichlorobromomethane levels through the Torresdale Plant O_3/GAC systems.

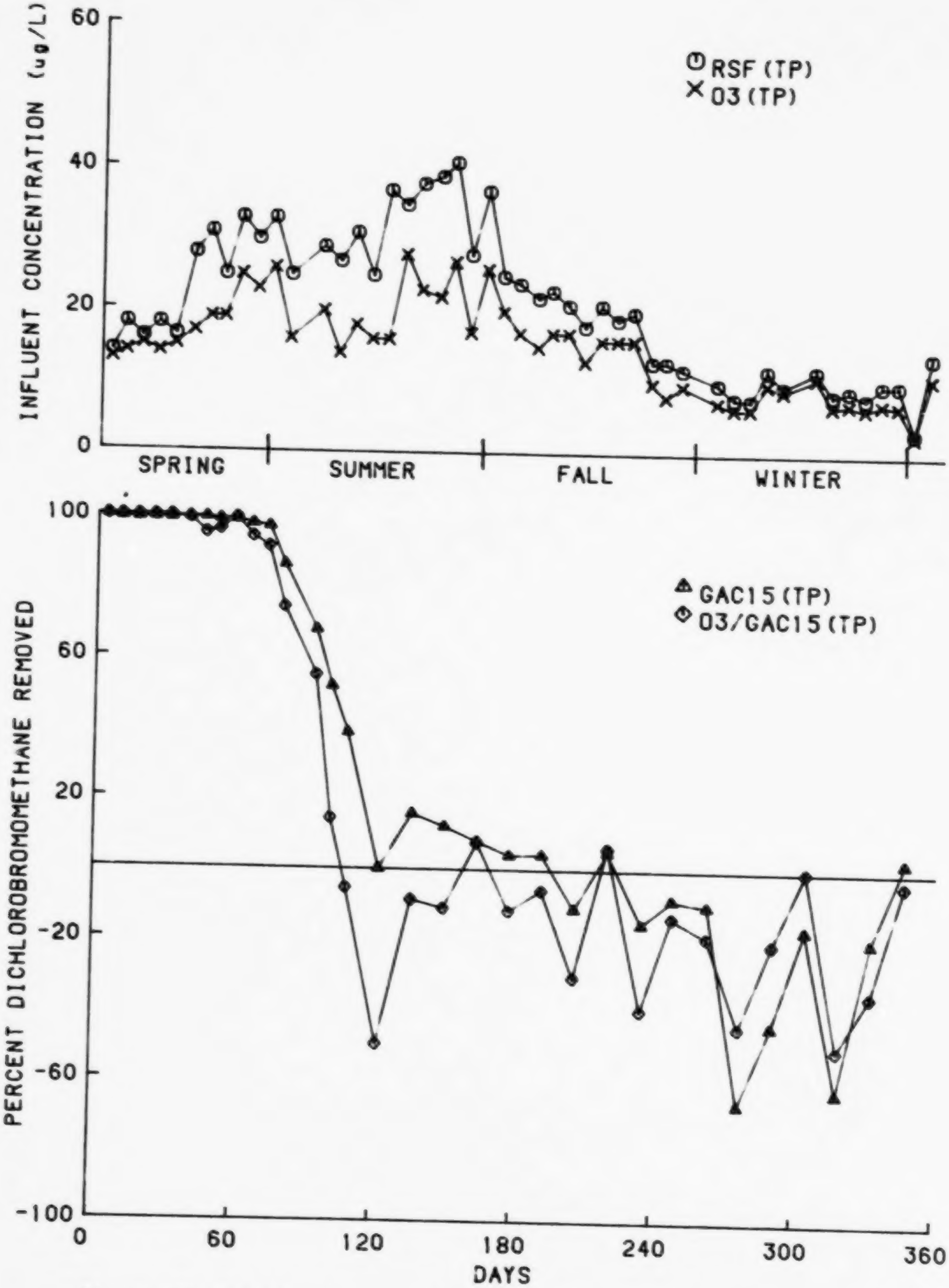

Figure 90. Dichlorobromomethane removal through the Torresdale Plant adsorption systems (15 min. EBCT).

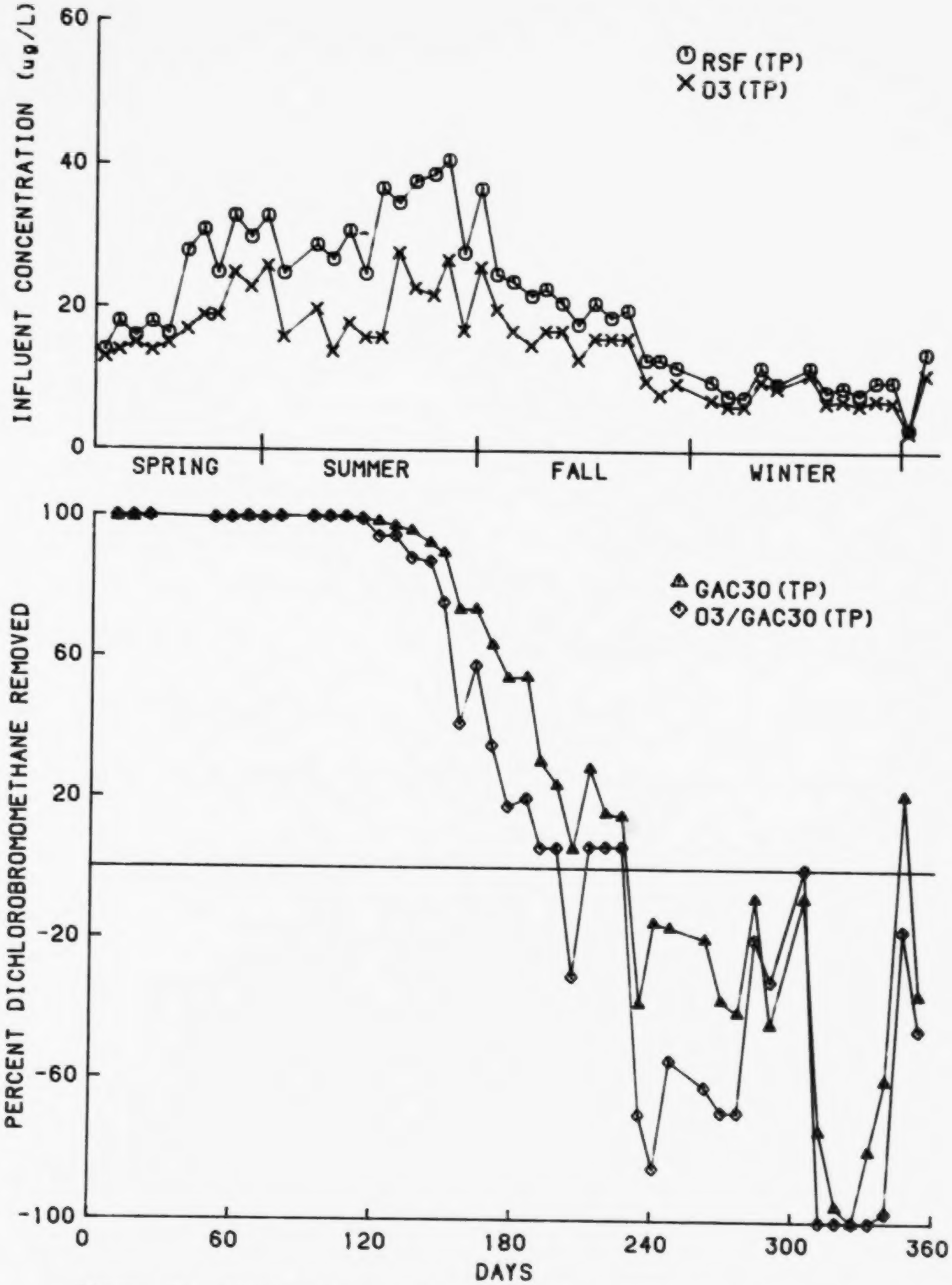

Figure 91. Dichlorobromomethane removal through the Torresdale Plant adsorption systems (30 min. EBCT).

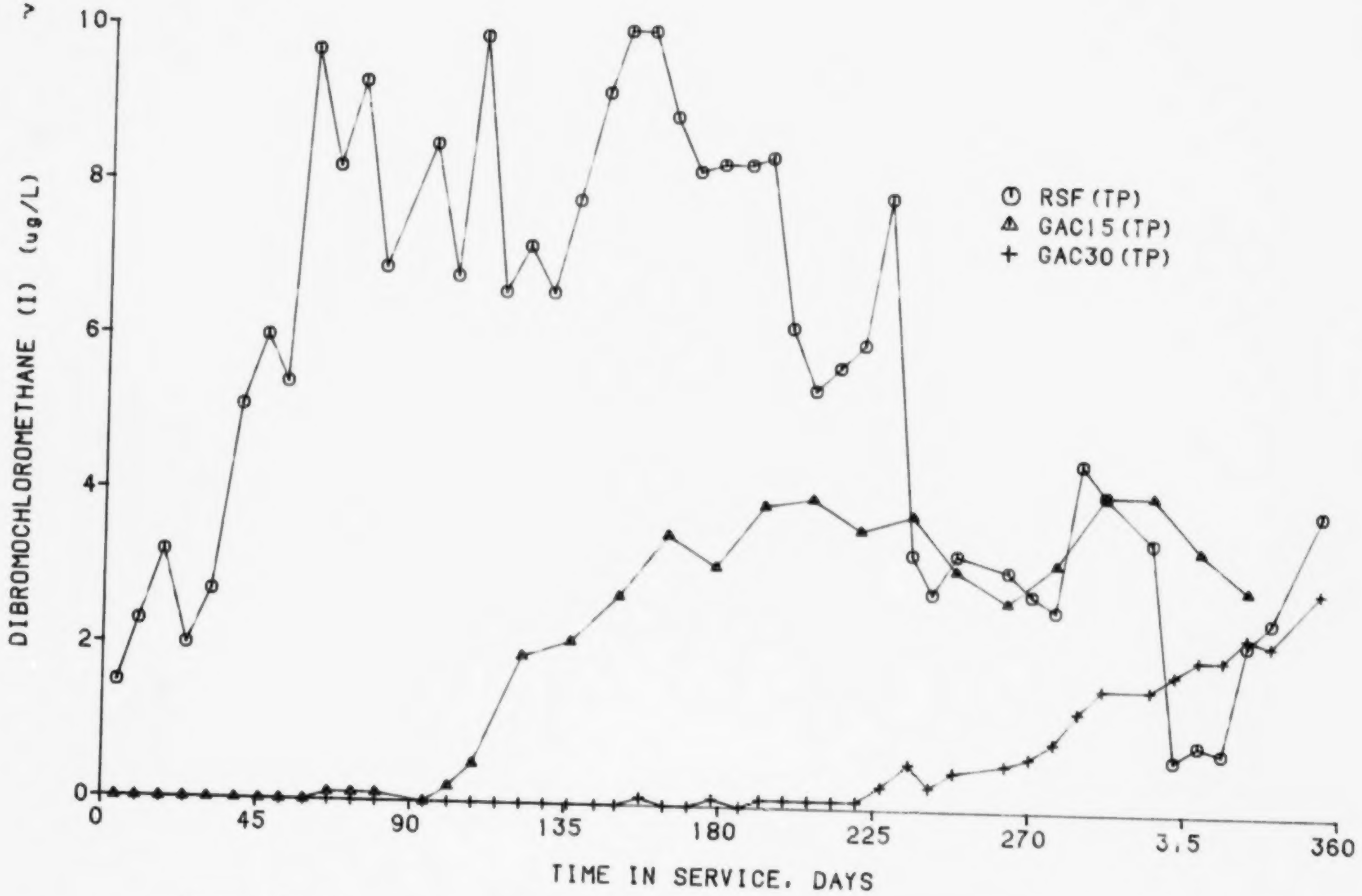

Figure 92. Dibromochloromethane levels through the Torresdale Plant GAC systems.

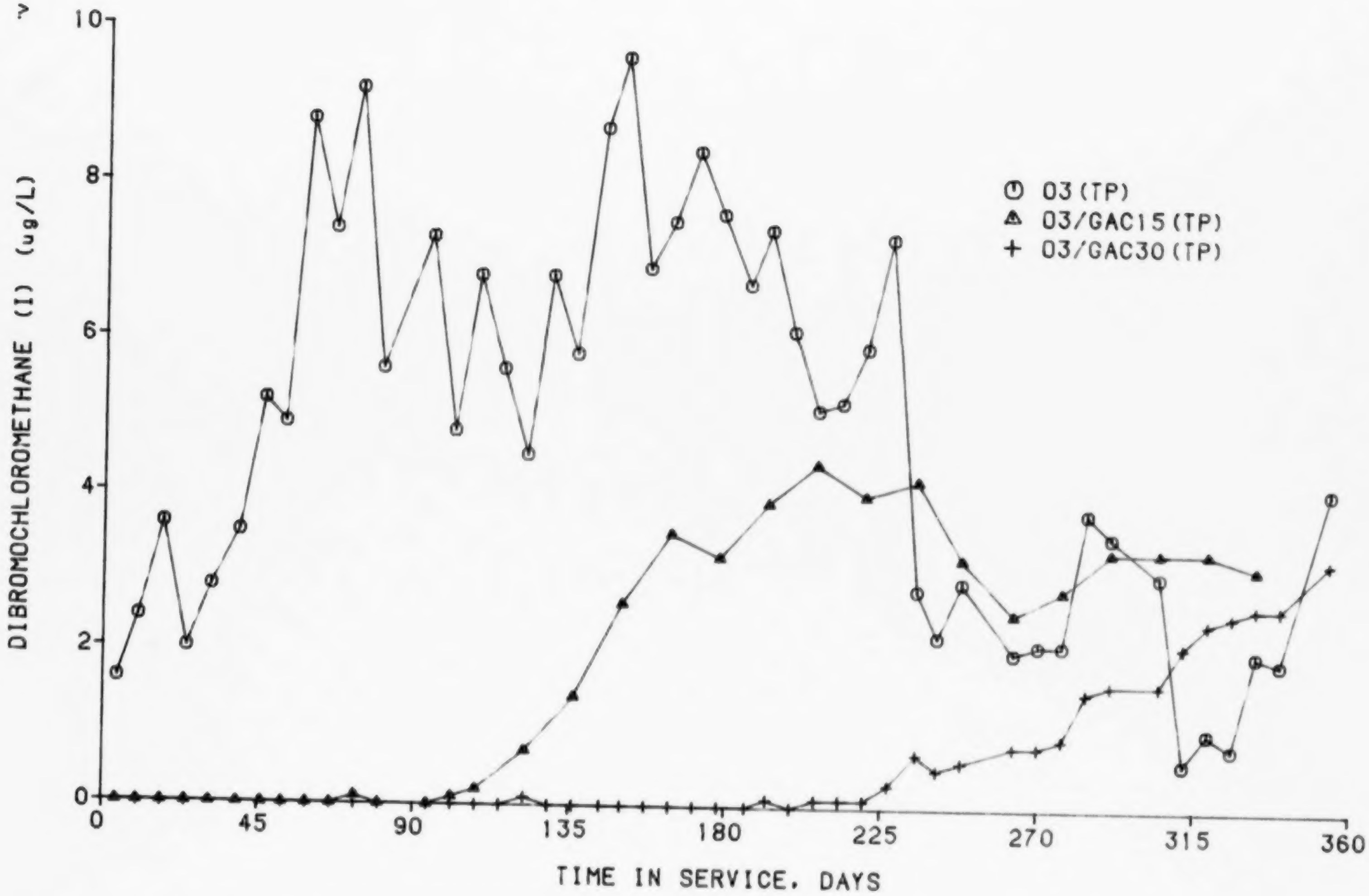

Figure 93. Dibromochloromethane levels through the Torresdale Plant O_3/GAC systems.

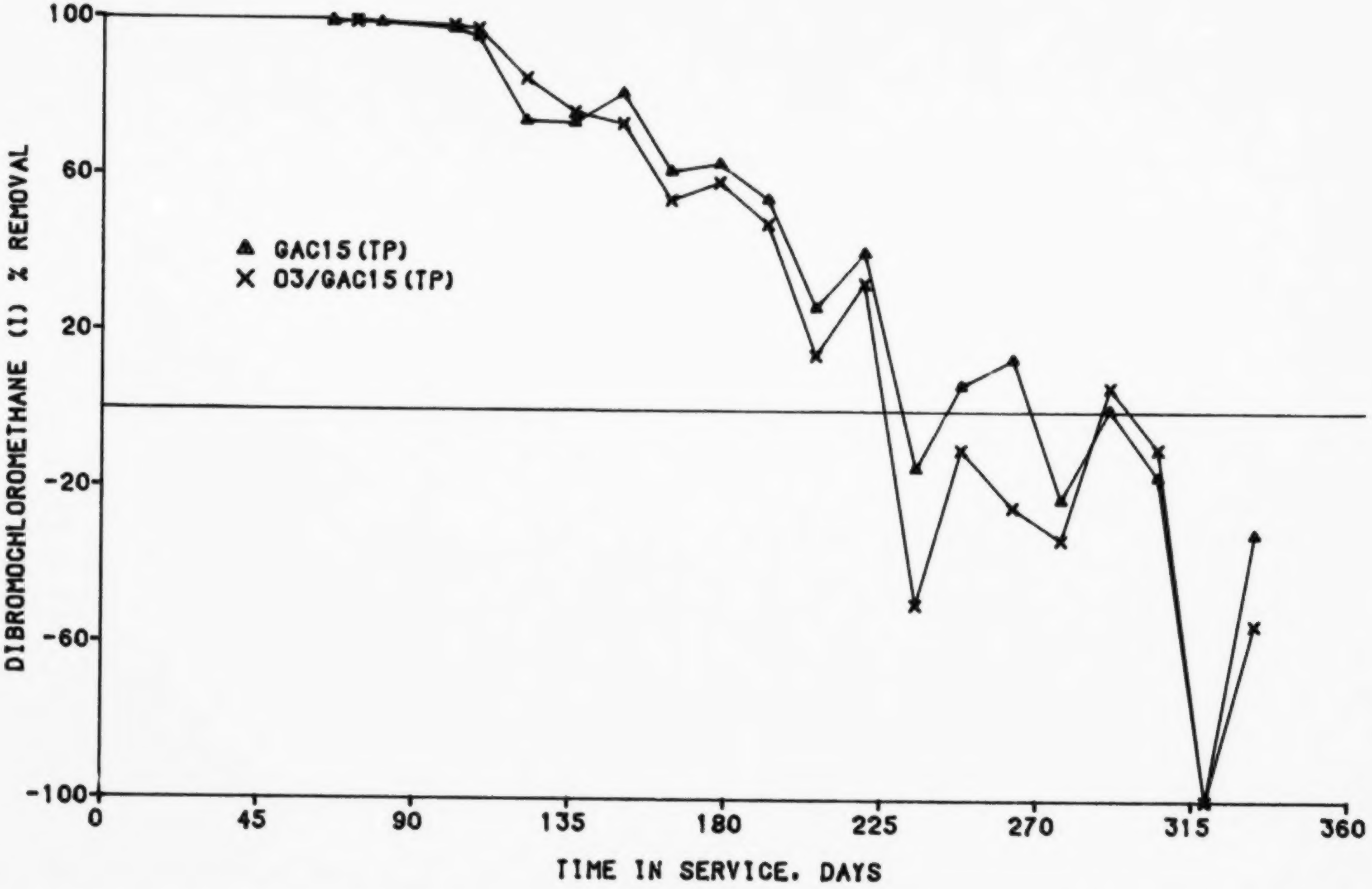

Figure 94. Dibromochloromethane removal through the Torresdale Plant adsorption systems (15 min. EBCT).

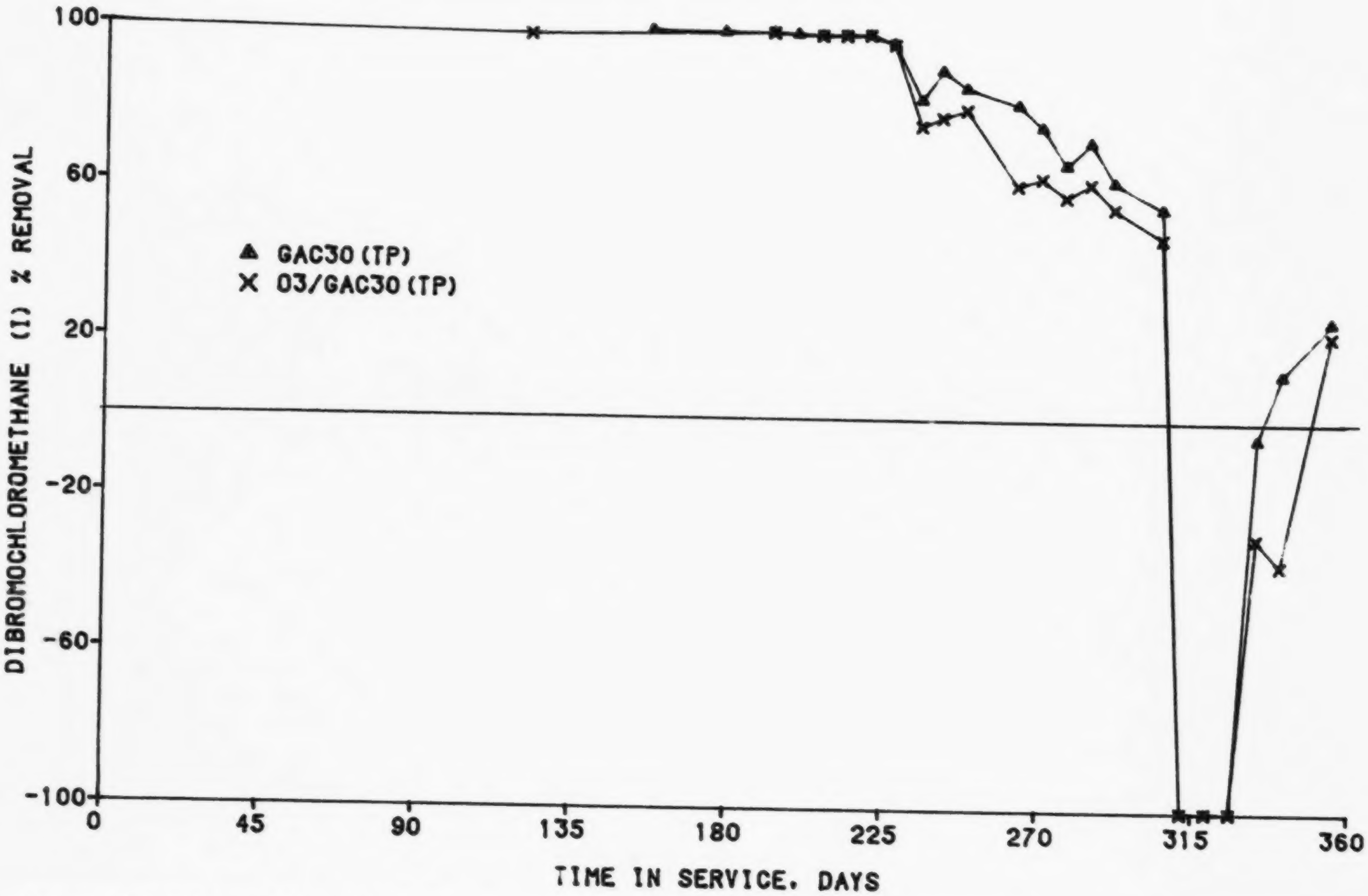

Figure 95. Dibromochloromethane removal through the Torresdale Plant adsorption systems (30 min. EBCT).

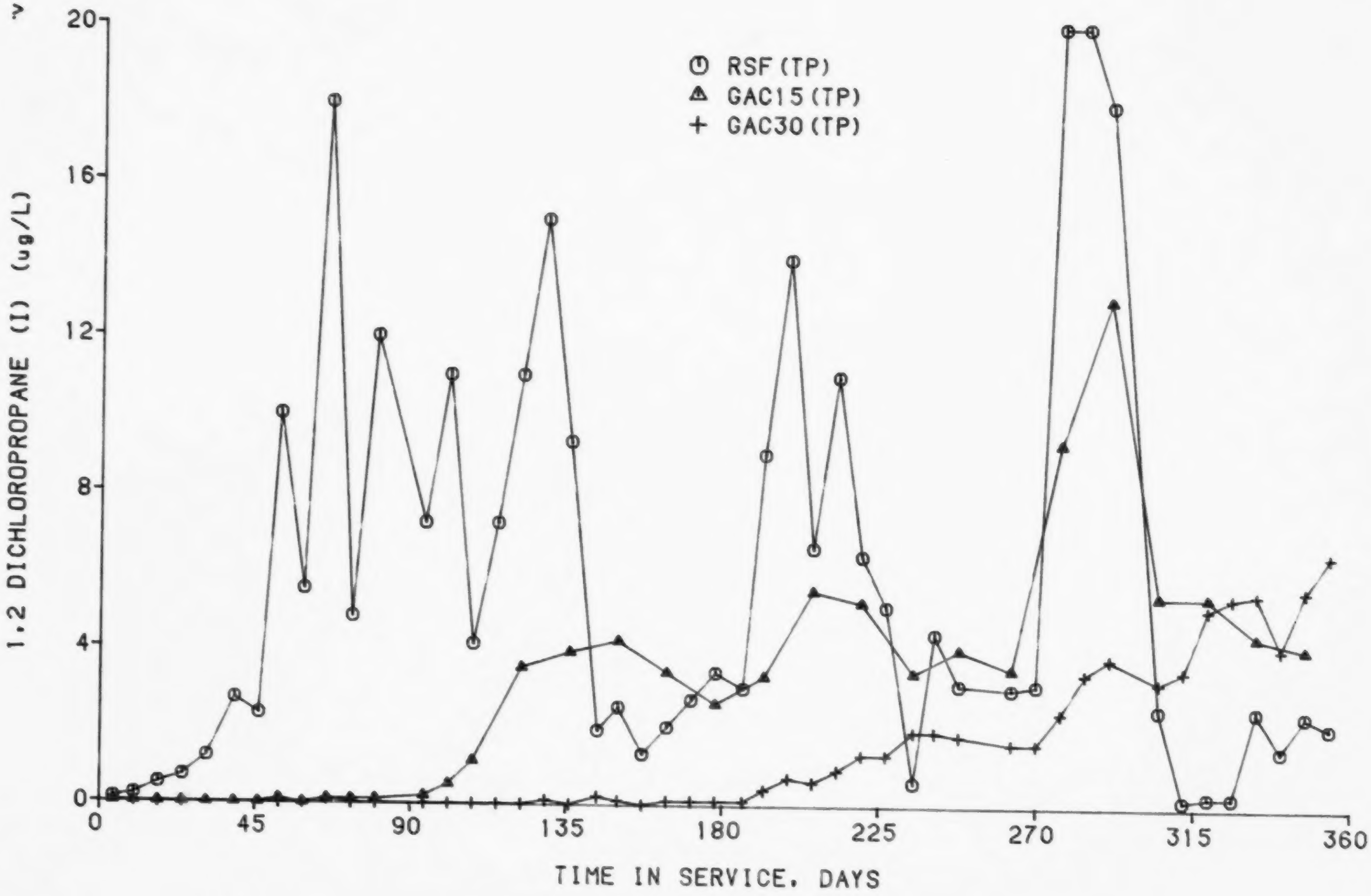

Figure 96. 1,2-Dichloropropane levels through the Torresdale Plant GAC systems.

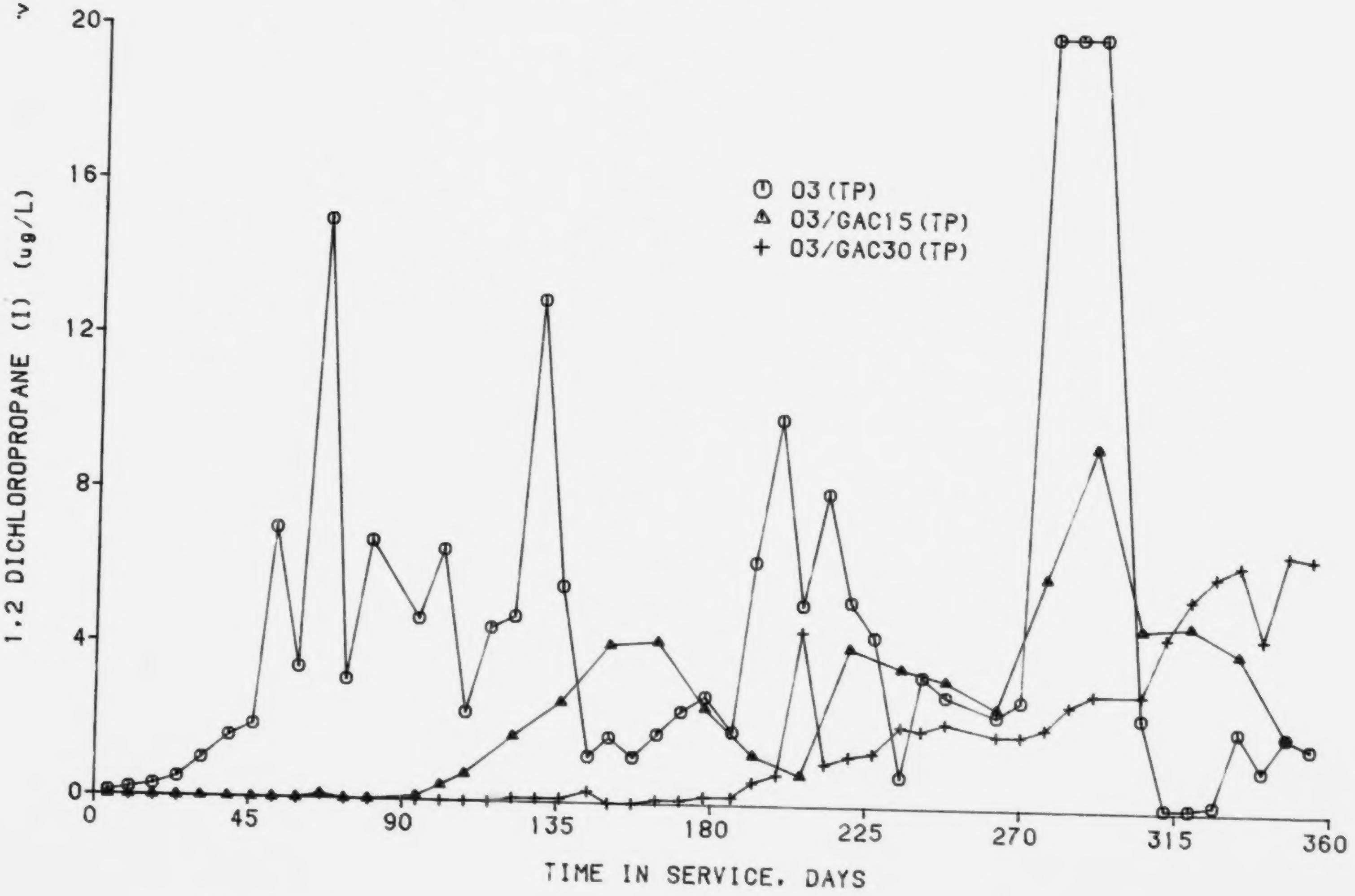

Figure 97. 1,2-Dichloropropane levels through the Torresdale Plant O_3/GAC systems.

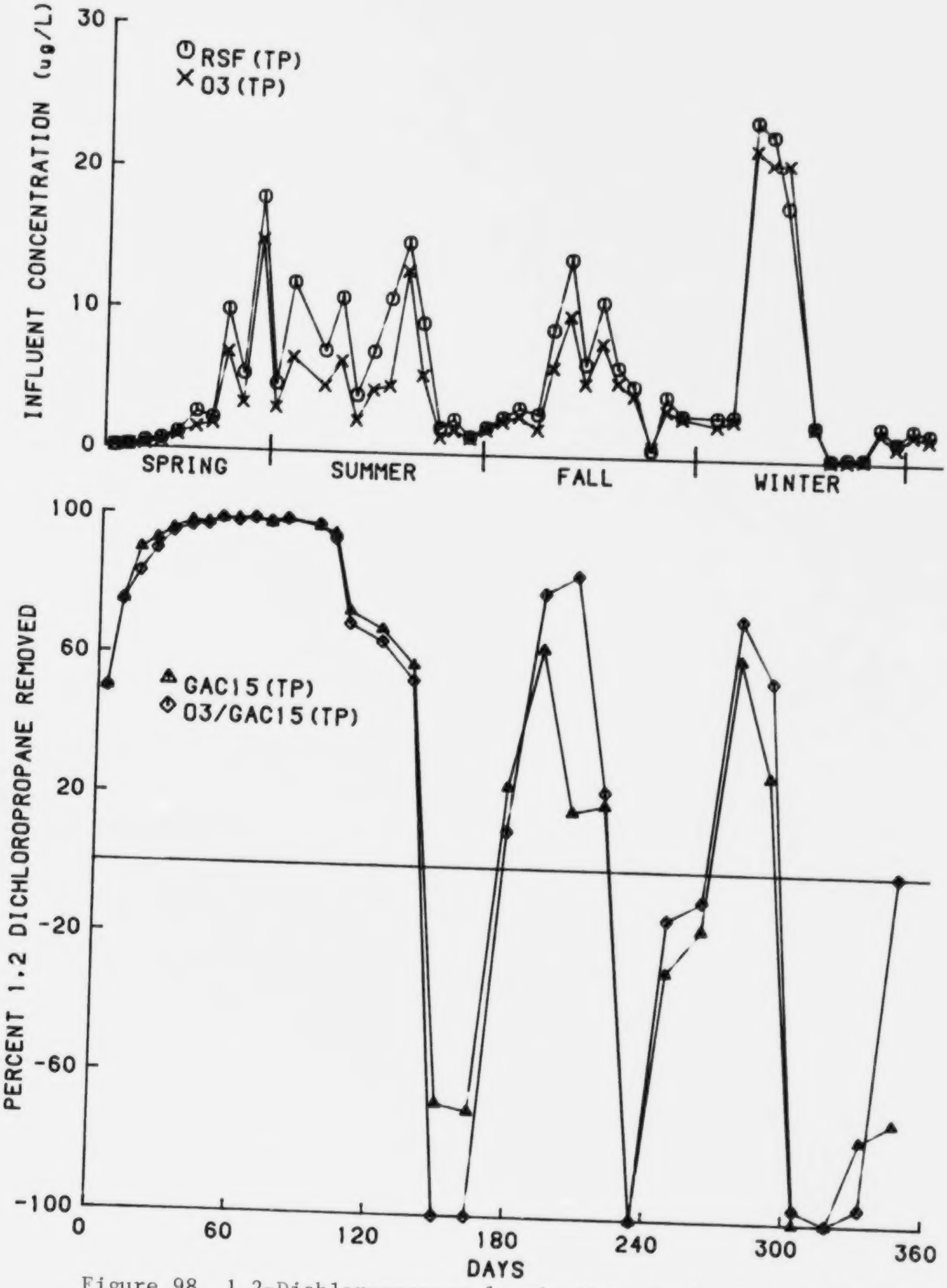

Figure 98. 1,2-Dichloropropane levels through the Torresdale Plant adsorption systems (15 min. EBCT).

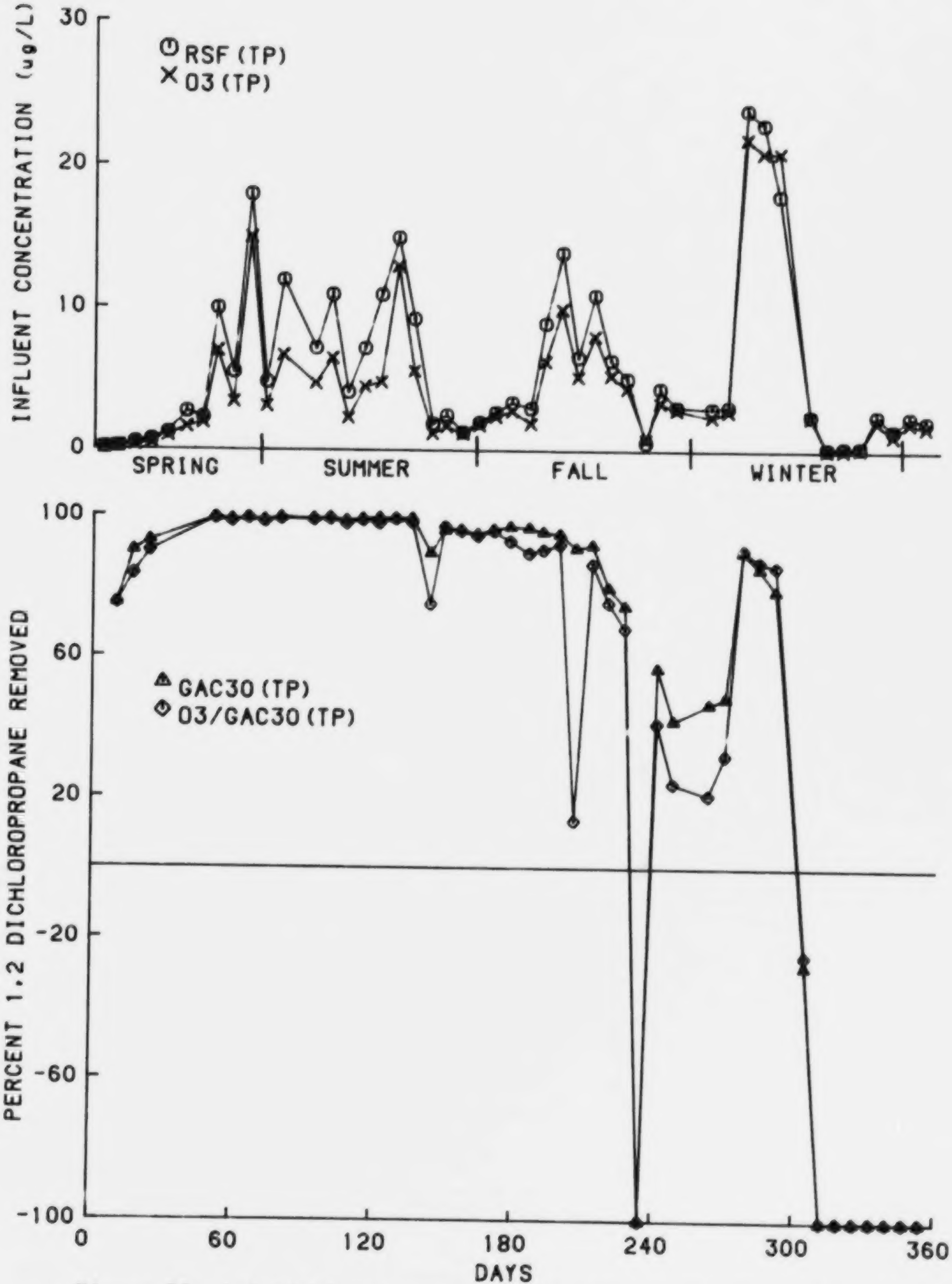

Figure 99. 1,2-Dichloropropane levels through the Torresdale Plant adsorption systems (30 min. EBCT).

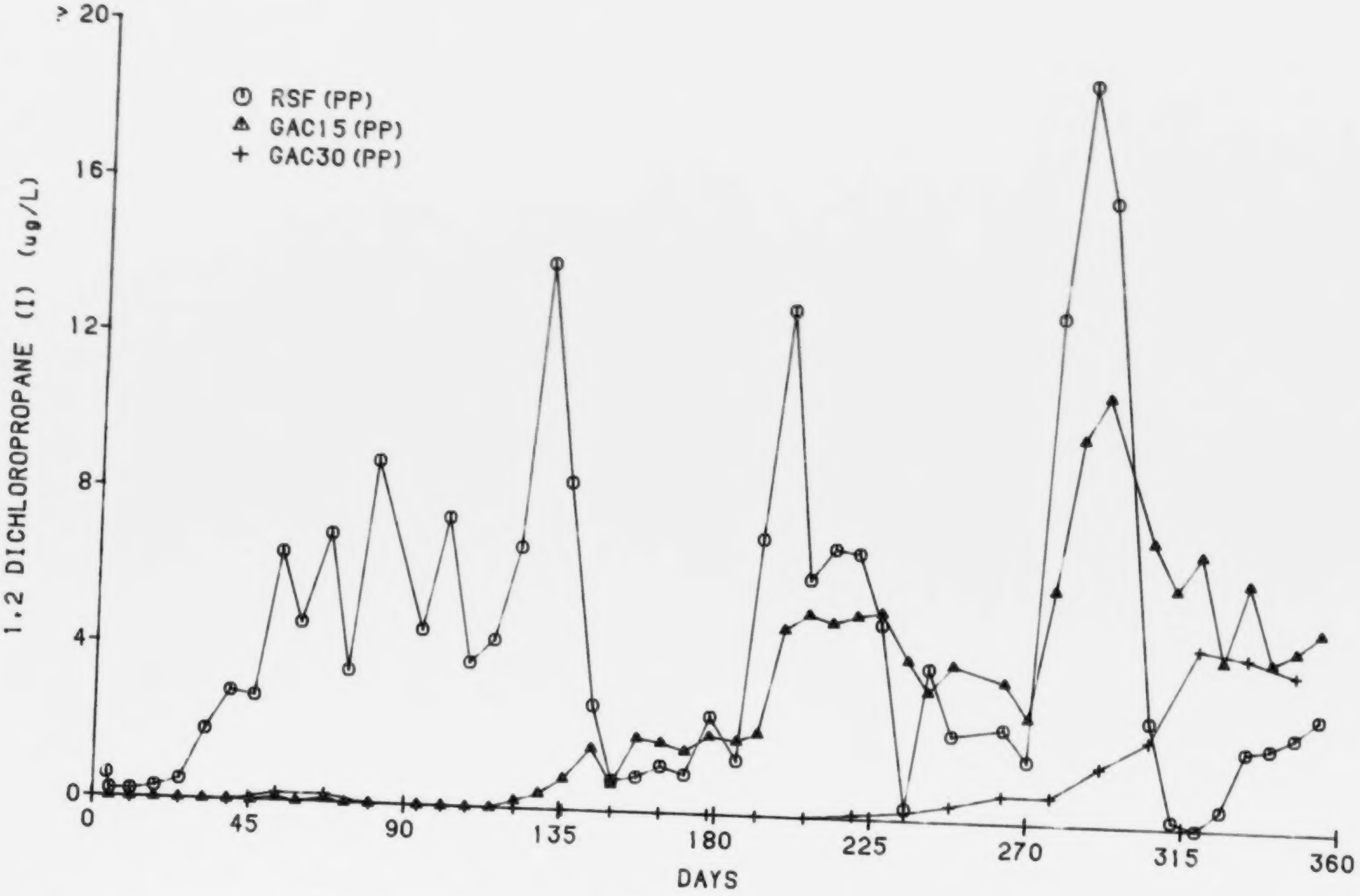

Figure 100. 1,2-Dichloropropane levels through the Pilot Plant GAC systems.

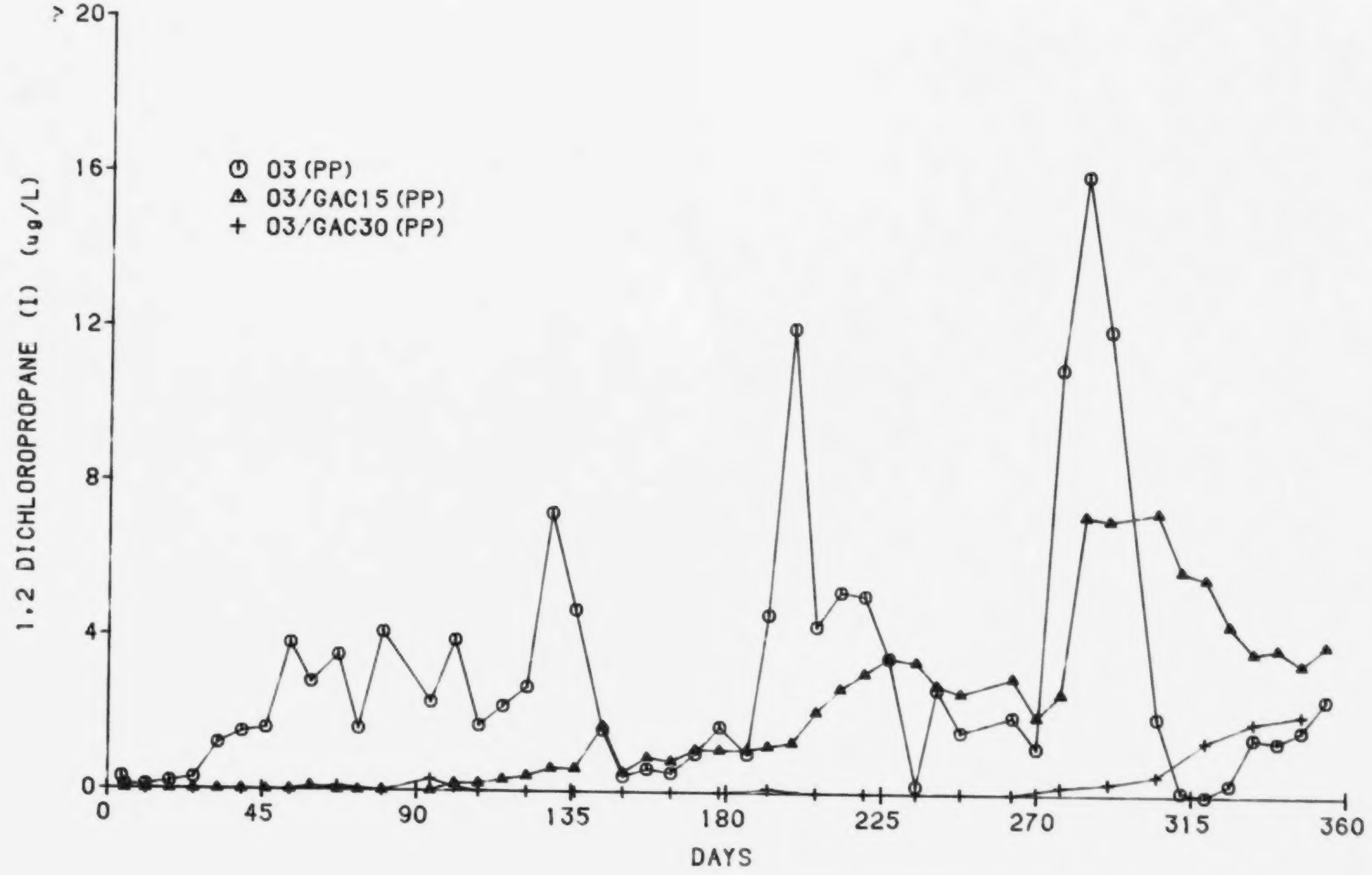

Figure 101. 1,2-Dichloropropane levels through the Pilot Plant O_3/GAC systems.

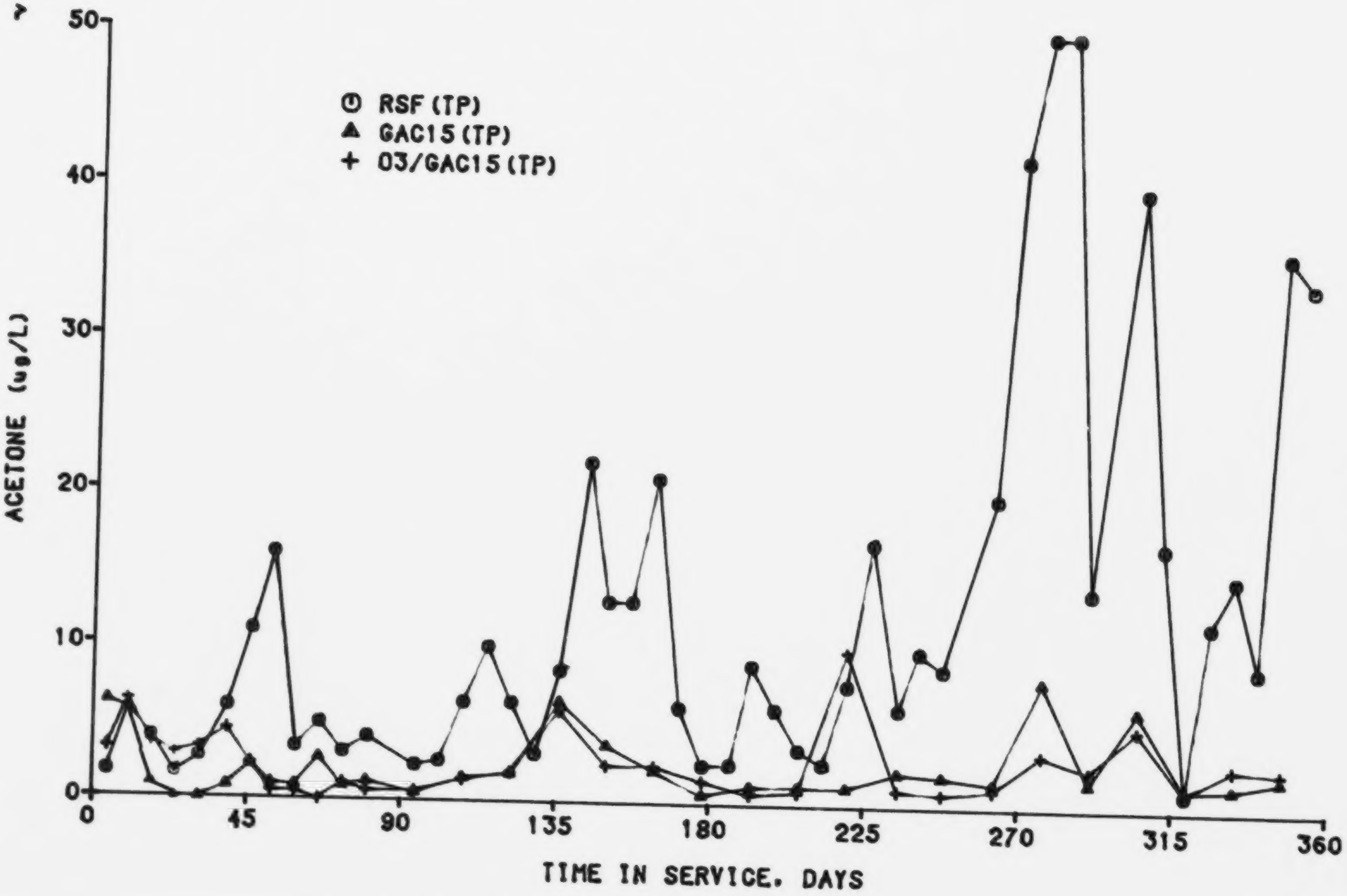

Figure 102. Acetone levels through the Torresdale Plant adsorption systems (15 min. EBCT).

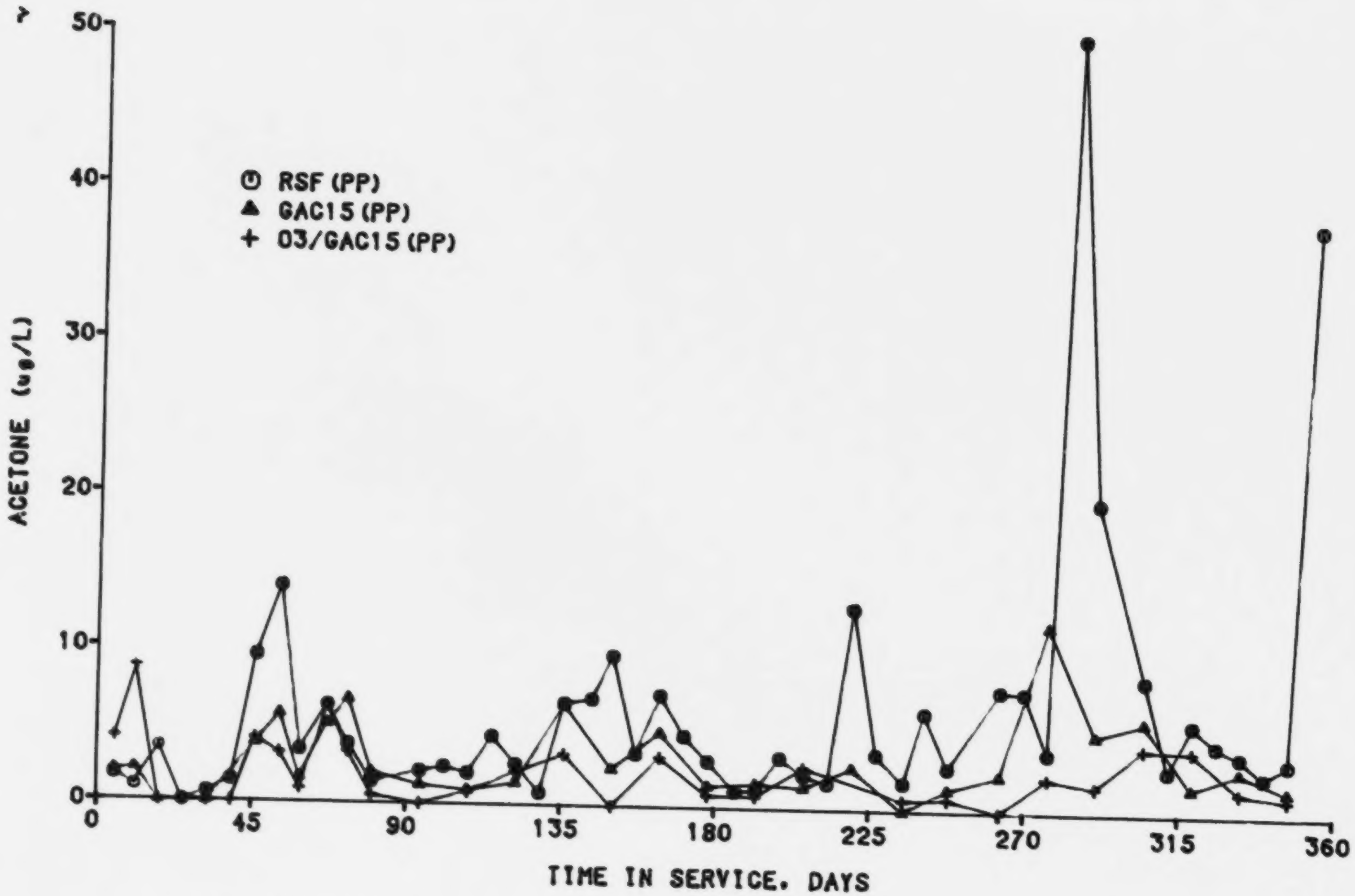

Figure 103. Acetone levels through the Pilot Plant adsorption systems (15 min. EBCT).

The only differences observed in this breakthrough hierarchy in the Torresdale Plant occurred through the preozonated GAC system where 1,2-DCE breakthrough is earlier than 1,2-DCP and carbon tetrachloride never reaches breakthrough. The CCl_4 difference may be explained by aeration in the ozone contactor reducing the average influent concentrations by 80%, thus bringing carbon tetrachloride levels to near the detection limits. Although the 1,2-DCP concentration was 20% lower than when entering the O_3/GAC system, this can not explain the entire discrepancy for 1,2-DCE. At the Pilot Plant, time to breakthrough of 1,2-DCP is equal to that of 1,2-DCE for the O_3/GAC system and is longer than 1,2-DCE for the GAC system. This is a similar transgression to that observed in the Torresdale Plant. The only other diversion from the above hierarchy was for trichloroethylene (after 37 and 42 weeks for the GAC and O_3/GAC systems, respectively). This compares to carbon tetrachloride and tetrachloroethylene where no breakthrough was observed during the study period. However, carbon tetrachloride breakthrough cannot be compared as it was primarily present only at the Torresdale Plant as an impurity in the chlorine gas. Also, 1,1,2,2-trichloroethylene was not observed in the Pilot Plant adsorption system effluents.

GC profiles from the broad spectrum analysis (C8 to C26 hydrocarbons) of samples collected by the MRR method were completed for the first 17 weeks at each GAC location. Figures 60 and 61 showed two exemplary sets of profiles from the Torresdale and Pilot Plants, respectively, for week five. The Torresdale and Pilot Plant GAC columns show 36-50% of the peaks in the effluent in the Kovats Index range of 800-1400 (C8-C14). This percentage increases after successive weeks on line. Table 43 showed that the types of compounds identified in the 800<KI<1400 range includes, C2- and C3-benzene isomers, C2- and C3-chlorobenzene isomers, aldehydes, ketones, nitriles, and thiazoles.

The data from this study confirms previous MRR data at Torresdale for GAC contactors. The previous studies show that as the GAC contactor remains on-line, the sequence of breakthrough is a function of increasing molecular weight for the non-polar trace organics of ng-ug/L concentration (34). Therefore the 800-1400 region of KI was chosen as a region of importance for the evaluation of GAC breakthrough for the first 17 weeks operation at the Pilot Plant.

Figures 104 and 105 show that complete breakthrough of organics never occurred for the Torresdale adsorption systems. Through week 8, the GAC system was somewhat more efficient than the O_3/GAC system. After week 8 the differences were not significant. As has been shown previously, the effluent levels appear to respond to changes in the influent levels.

A comparison of Figures 104 and 106 show that the sum of influent peak area (800<KI<1400) and number of peaks are lower for the Pilot Plant GAC contactors as compared to the Torresdale Plant GAC contactors. Yet, the effluent peak area (but not the number of peaks) from the carbon contactors from both the Pilot Plant and Torresdale Plant are approximately the same after the first 7 weeks. A comparison of Figures 105 and 107 show that the Pilot Plant O_3/GAC and GAC contactors follow each other up to week 10. Also, the effluent levels do not appear to respond to changes in influent levels for

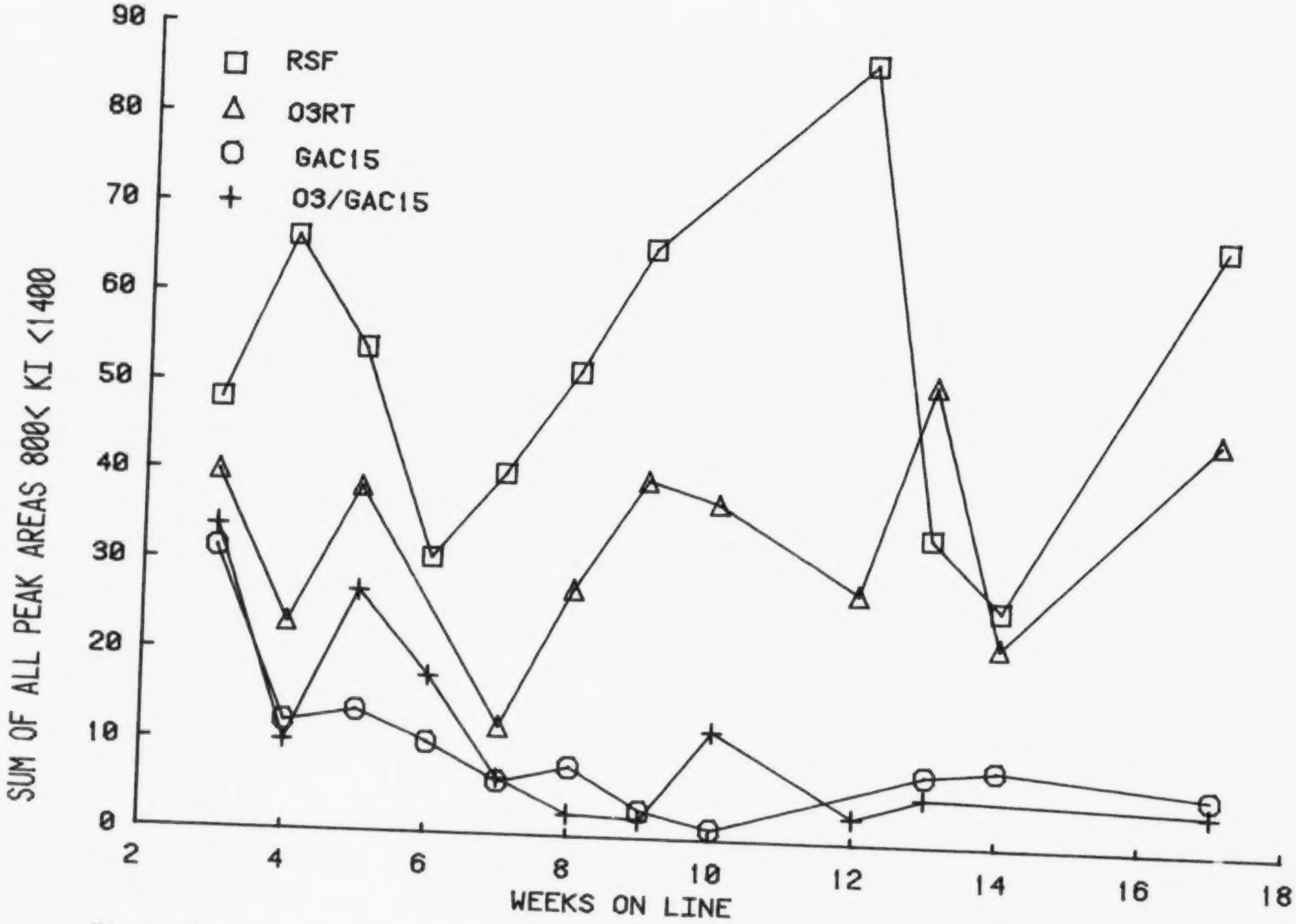

Figure 104. The effect of ozonation on Torresdale Plant GAC nonpolar trace organics.

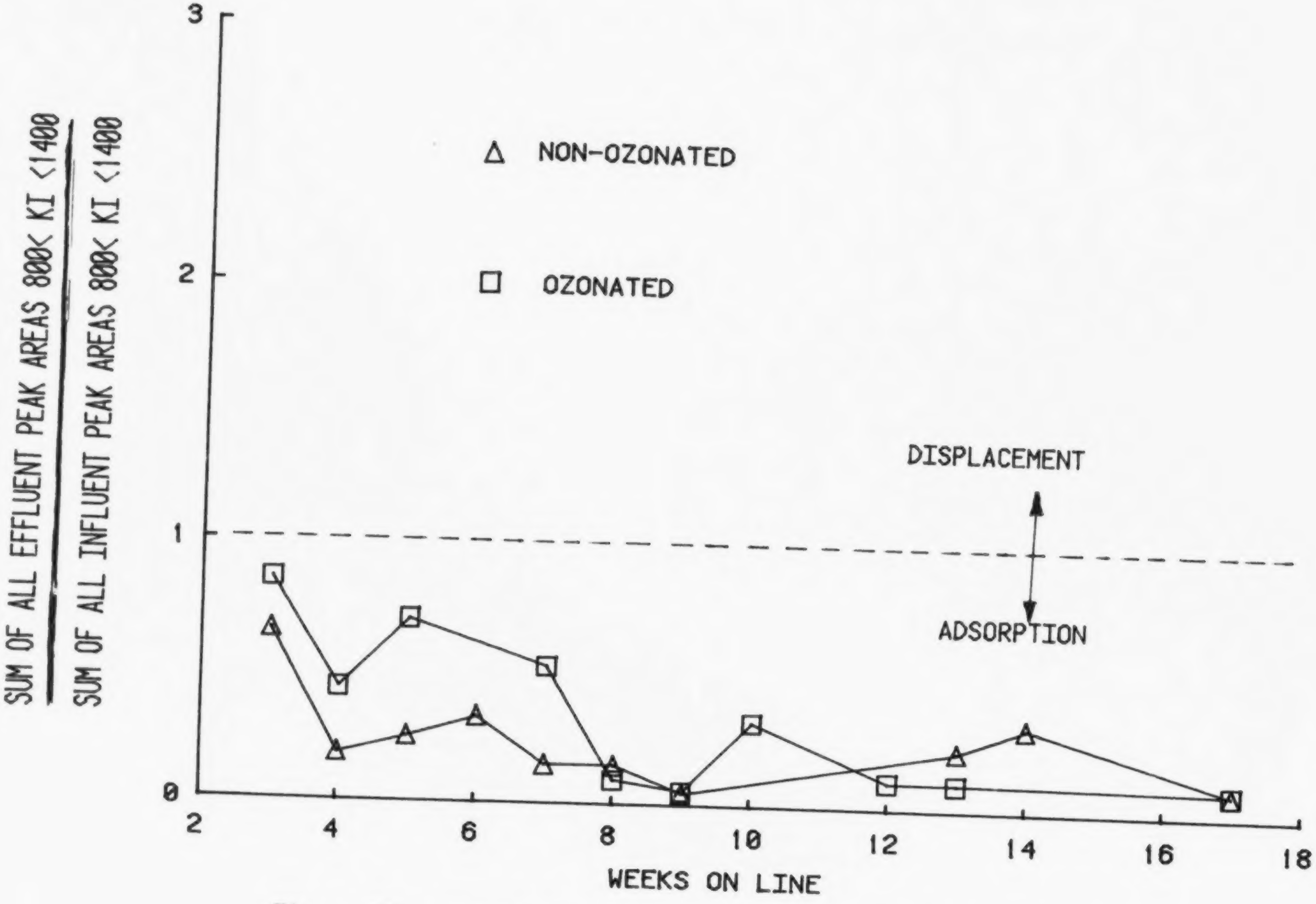

Figure 105. Torresdale GAC contactor performance for nonpolar organics.

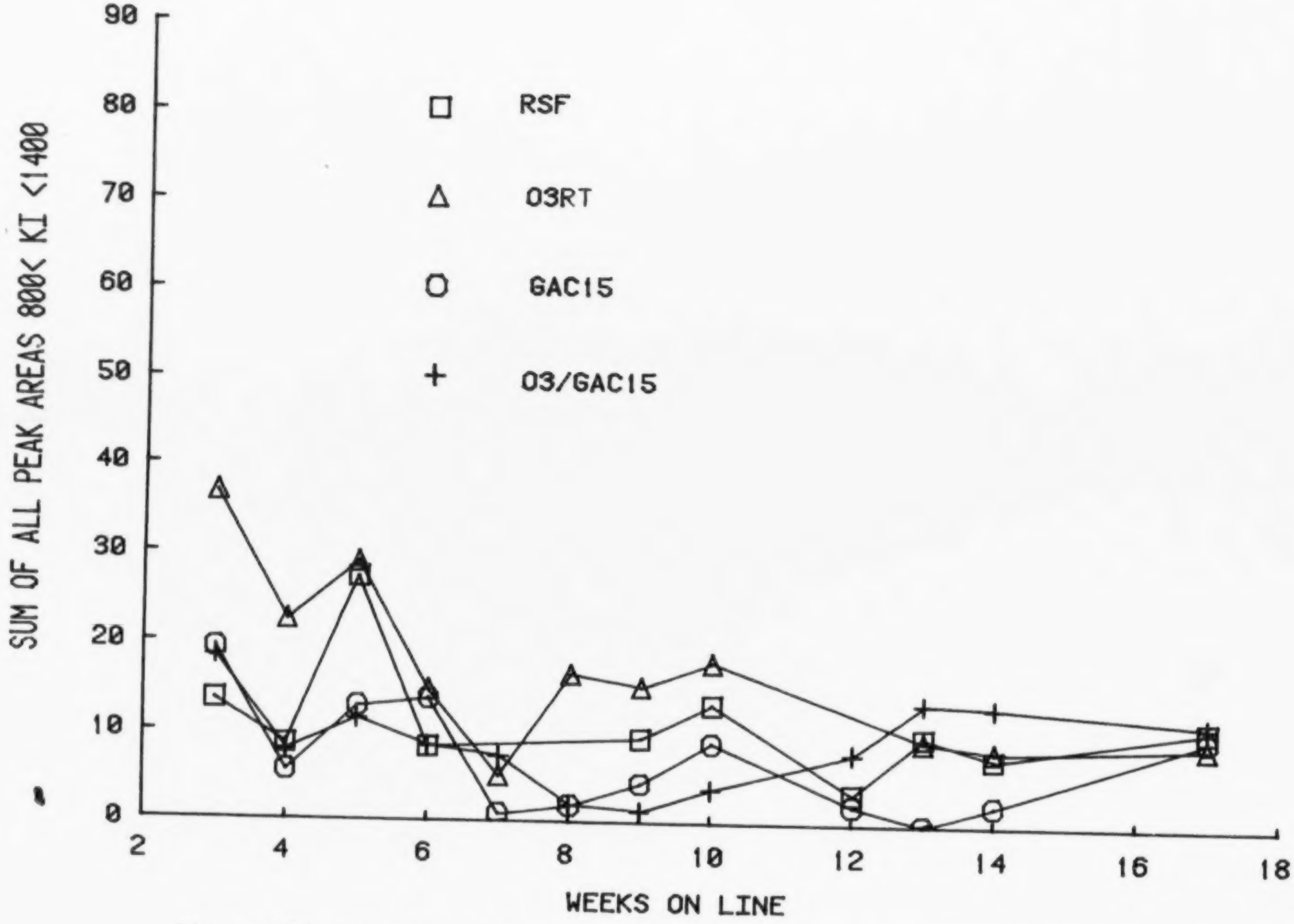

Figure 106. The effect of ozonation on Pilot Plant GAC nonpolar trace organics.

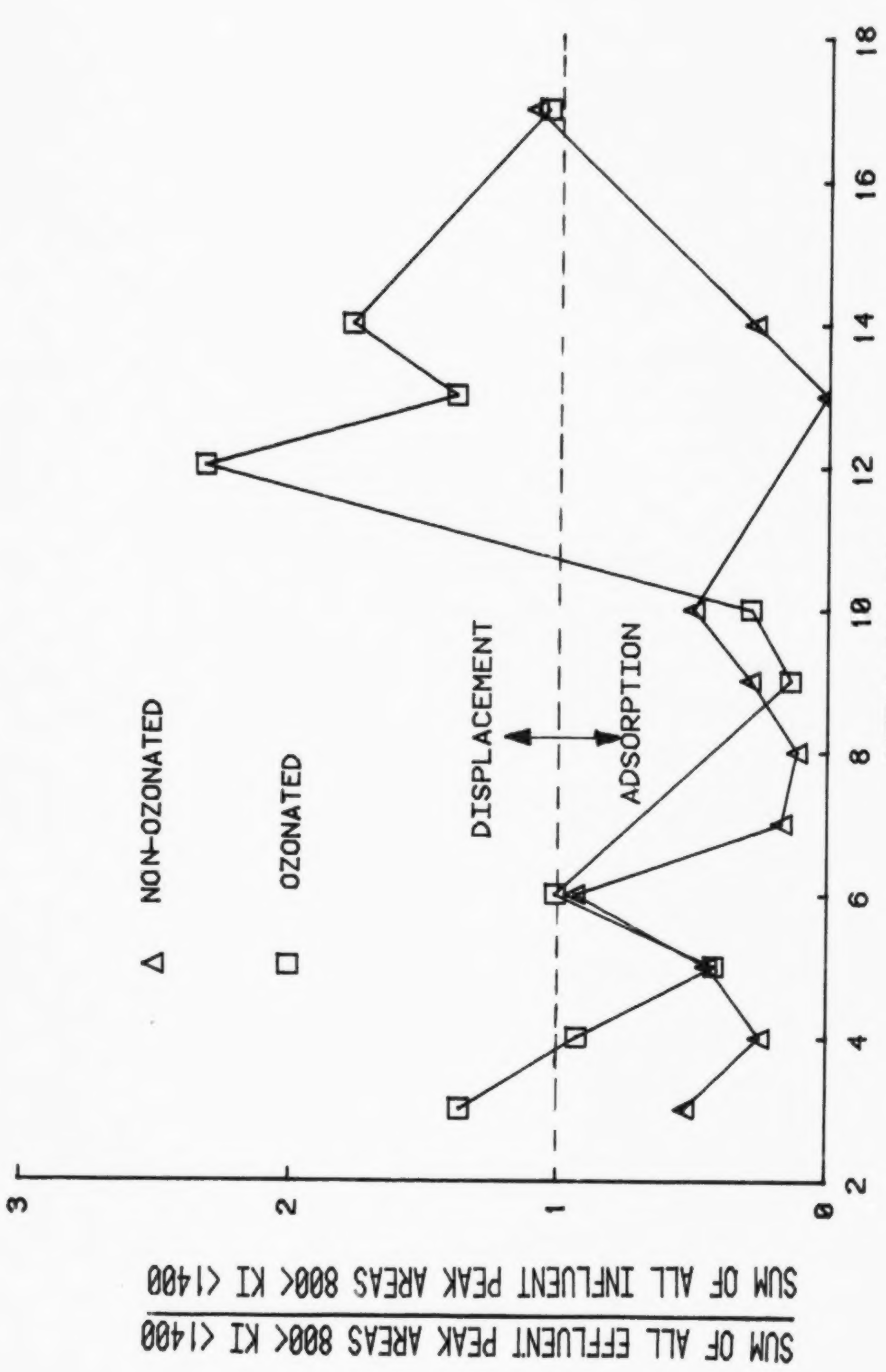

Figure 107. Pilot Plant GAC contactor performance for nonpolar organics.

both Pilot Plant GAC contactors up to week 10.

Figure 107 shows that the effluent levels of the O_3/GAC Pilot Plant system were higher than the influent levels from weeks 10 through 17. Displacement is apparent. This is a chromatographic effect. On the otherhand, the GAC column maintains its adsorption capacity up to week 17 at which time the effluent is slightly greater than the influent.

This data set indicates that the ozonation process significantly alters the character of the trace organics present in the Pilot Plant influent but not the chlorinated influent at Torresdale which remains consistent for O_3/GAC vs GAC. The prechlorination process apparently forms compounds which are not readily oxidized by ozone. The breakthrough of an increasing number of compounds occurs slowly with time in the prechlorinated waters.

Figure 108 shows the breakthrough of the higher molecular weight compounds (KI>1400) at the Pilot Plant. No chromatographic effect was apparent, indicating that higher molecular weight organics do not effect displacement of the lower molecular weight organics. Figures 107 and 108 show that from week 13 on, a displacement effect occurs for the entire MW range of 800 to 2600.

Ozone/Sand System--

General Organics--DOC levels through the $O_3/SAND_{15}$ system for the first year of the pilot-scale studies were presented previously (Figure 46). These results were presented along with those of the ozonation system in order to provide a means of measuring the effectiveness of the ozonation process for producing biodegradable organics. Minicolumn work (to be presented later in this section) shows that the DOC removal observed through the sand bed is equivalent to the DOC removal due to biodegradation on a carbon bed. By comparing the results of the parallel $O_3/SAND_{15}$(PP) and the O_3/GAC_{15}(PP) systems, therefore, a determination may be made as to the relative contributions of adsorption and biodegradation to DOC removal on GAC.

Figure 109 presents DOC levels in the effluents of the Pilot Plant rapid sand filters, the $O_3/SAND_{15}$ system and the O_3/GAC_{15} system. The time period shown is between days 200 to 600, when steady-state conditions prevailed in the O_3/GAC_{15} system. It is evident from this graph that DOC levels in the O_3/GAC_{15} effluent were consistently lower than in the $O_3/SAND_{15}$ effluent, indicating that adsorption still plays a role in organic removal after 18 1/2 months of system operation.

Specific Organics--A comparison of trace organics present in the influent and effluent of the sand bed shows that, out of nine sampling periods tested, only one had a significantly different effluent from influent (using the MRR extraction method, with $p = 0.05$). These results indicate that the sand bed does not have much effect on the non-polar organics which the broad spectrum analysis is designed to measure. This is an expected result since these compounds are not readily biologically degraded.

Ozone/Sand Studies--

During the final 6 1/2 months of the project period, five ozone/sand

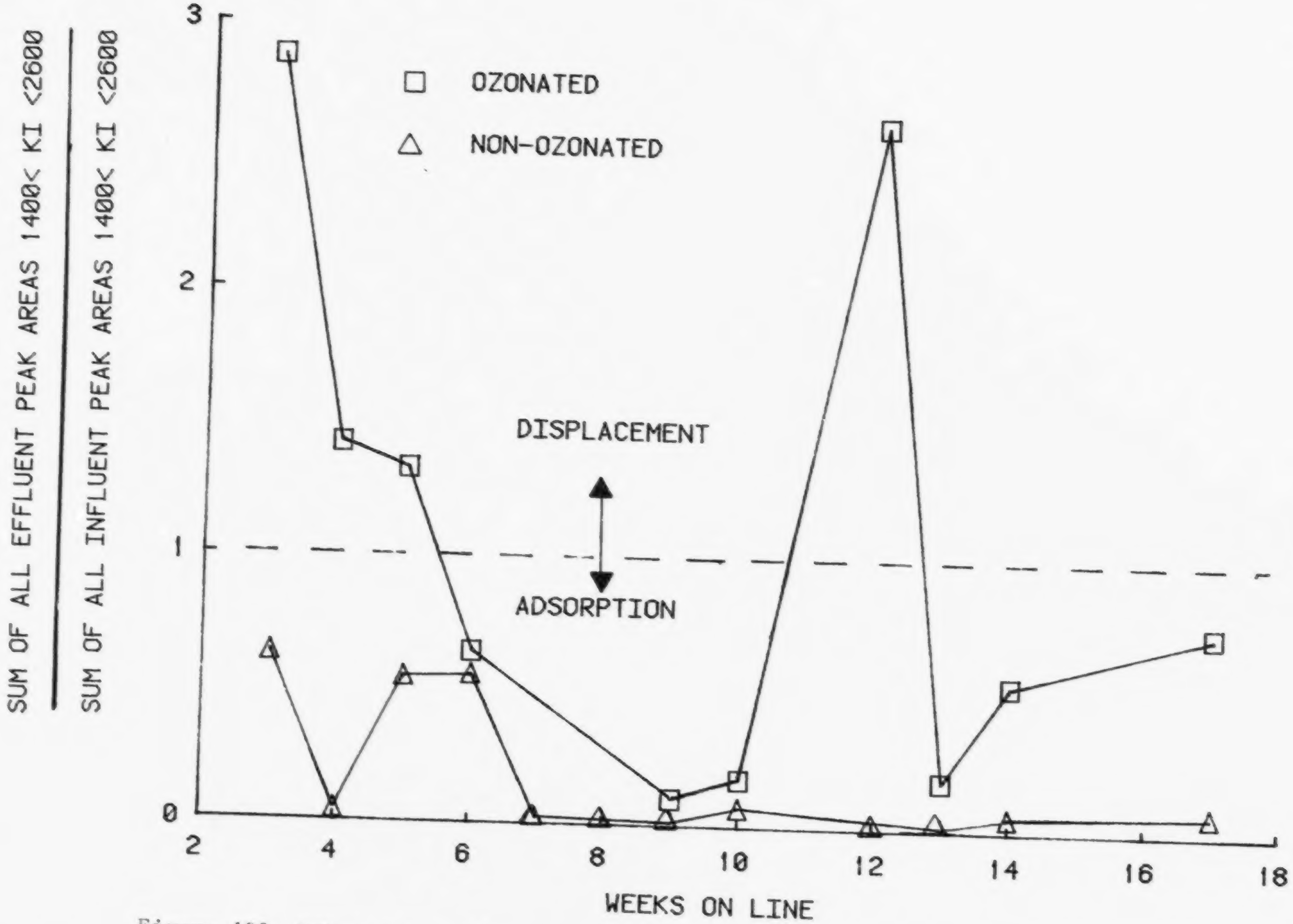

Figure 108. Pilot Plant GAC contactor performance for nonpolar organics (KI<1400).

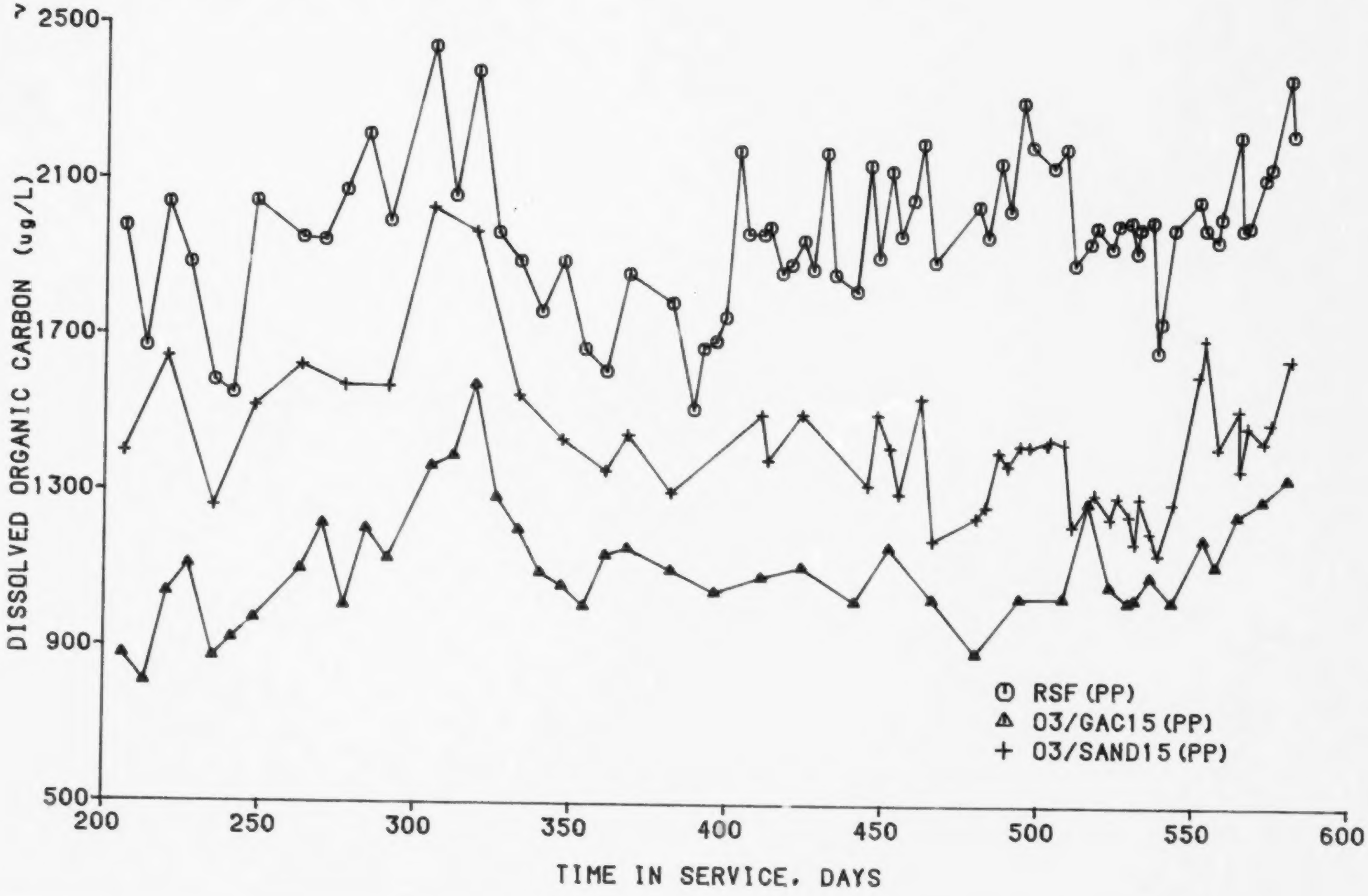

Figure 109. Steady state DOC removal through the Pilot Plant O_3/GAC and O_3/SAND systems (15 min. EBCT).

studies were conducted. Each study investigated the comparative performance of two ozone contactors and their associated sand beds. Both ozone contactors were applied with Pilot Plant rapid sand filter effluent. One of the $O_3/SAND_{15}$ systems, the control, was operated under the same conditions and in the same mode throughout the study period. The other $O_3/SAND_{15}$ system, the experimental system, was operated under varying conditions, depending on the study being conducted. Figure 13 and Table 7 show the sampling locations for these studies.

The goals of the five $O_3/SAND_{15}$ studies were to gain a better understanding of the ozone contacting and the $O_3/SAND_{15}$ systems and to determine the feasibility of incorporating an $O_3/SAND$ system into the operation of a conventional water treatment plant. Since no adsorptive forces were at work in these studies, the results obtained for the surrogate organic parameters (DOC, THMFP and A254) were stressed. Measurements were gathered at the Pilot Plant rapid sand filter effluent (influent to the two ozone contactors), the two ozone retention tank effluents, and the effluent from each of the sand columns. A brief description of each study and its results follows.

Ozone Contactor Performance Comparison--The objective of the first ozone/sand study was to determine whether the two ozone systems would yield equivalent results if run under identical operating conditions. This experiment was important in order to confirm that the differences noted between the Torresdale and Pilot Plant ozonation systems were due to differences in the applied water and not due to differences in the operating characteristics of the two contactors.

DOC, THMFP, and A254 absorbance levels through the two ozonation systems are presented in Figures 110 through 112, respectively. The results, summarized in Table 57, indicate that the two contactors did, in fact, perform equivalently. It is interesting to note that while the majority of the reduction in A254 absorbance levels occurred within the ozone contactor, DOC and THMFP levels were also reduced through the sand beds. In determining the effectiveness of ozone as a pretreatment to GAC adsorption, the reduction of organics to biodegradable forms is as important as the complete oxidation of organics to carbon dioxide.

Contact Time Comparison--The objective of the second study was to determine the influence of ozone/water contact time on the oxidation of organic compounds. This was accomplished by doubling the contact time in the experimental ozone contactor and comparing changes in DOC, THMFP and A254 absorbance levels with those through the control system. The results are presented in Figures 113 to 115 and are summarized in Table 58.

The results indicate that an increase in contact (or reaction) time will result in additional reductions in DOC, THMFP and A254 absorbance levels. DOC appeared to be the most sensitive parameter to changes in the contact time. It is interesting to note that most of the additional removal occurred within the ozone contactor; additional reaction time did not appear to affect the biodegradable portion of the DOC, THMFP or A254 absorbing compounds.

Contact Time and Dosage Comparison--With the contact time still doubled,

TABLE 57. O_3/SAND STUDY #1 (CONTACTOR COMPARISON)

PARAMETER	RSF	CONTROL SYSTEM				EXPERIMENTAL SYSTEM			
		OZONE CONTACTOR		SAND BED		OZONE CONTACTOR		SAND BED	
		Amount	%Δ	Amount	%Δ	Amount	%Δ	Amount	%Δ
DOC(ppb)	1881	1687	10.3	1443	23.3	1718	8.7	1457	22.5
THMFP(ppb)	133	107	19.5	87	34.6	108	18.8	92	30.8
A254	0.194	0.103	46.9	0.104	46.4	0.108	44.3	0.109	43.8
OZONE		CONTROL SYSTEM				EXPERIMENTAL SYSTEM			
-Dose(mg/l)		1.2				1.2			
-Contact Time(min)		22				22			
-Utilized(mg/l)		1.92				1.99			

Study Period-5/5/81 to 6/20/81

Both systems use PP RSF effluent as water source.

%Δ based on RSF effluent

TABLE 58. O_3/SAND #2 (CONTACT TIME COMPARISON)

PARAMETER	RSF	CONTROL SYSTEM				EXPERIMENTAL SYSTEM			
		OZONE CONTACTOR		SAND BED		OZONE CONTACTOR		SAND BED	
		Amount	%Δ	Amount	%Δ	Amount	%Δ	Amount	%Δ
DOC(ppb)	2014	1737	13.8	1349	33.0	1528	24.1	1163	42.3
THMFP(ppb)	141	109	22.7	87	38.3	104	26.2	84	40.4
A254	0.194	0.089	54.1	0.084	56.7	0.076	60.8	0.068	64.9
OZONE		CONTROL SYSTEM				EXPERIMENTAL SYSTEM			
-Dose(mg/1)		1.5				1.5			
-Contact Time(min)		22				44			
-Utilized(mg/1)		2.6				4.36			

Study Period-6/21/81 to 7/21/81

Both systems use PP RSF Effluent as water source.

%Δ based on RSF effluent

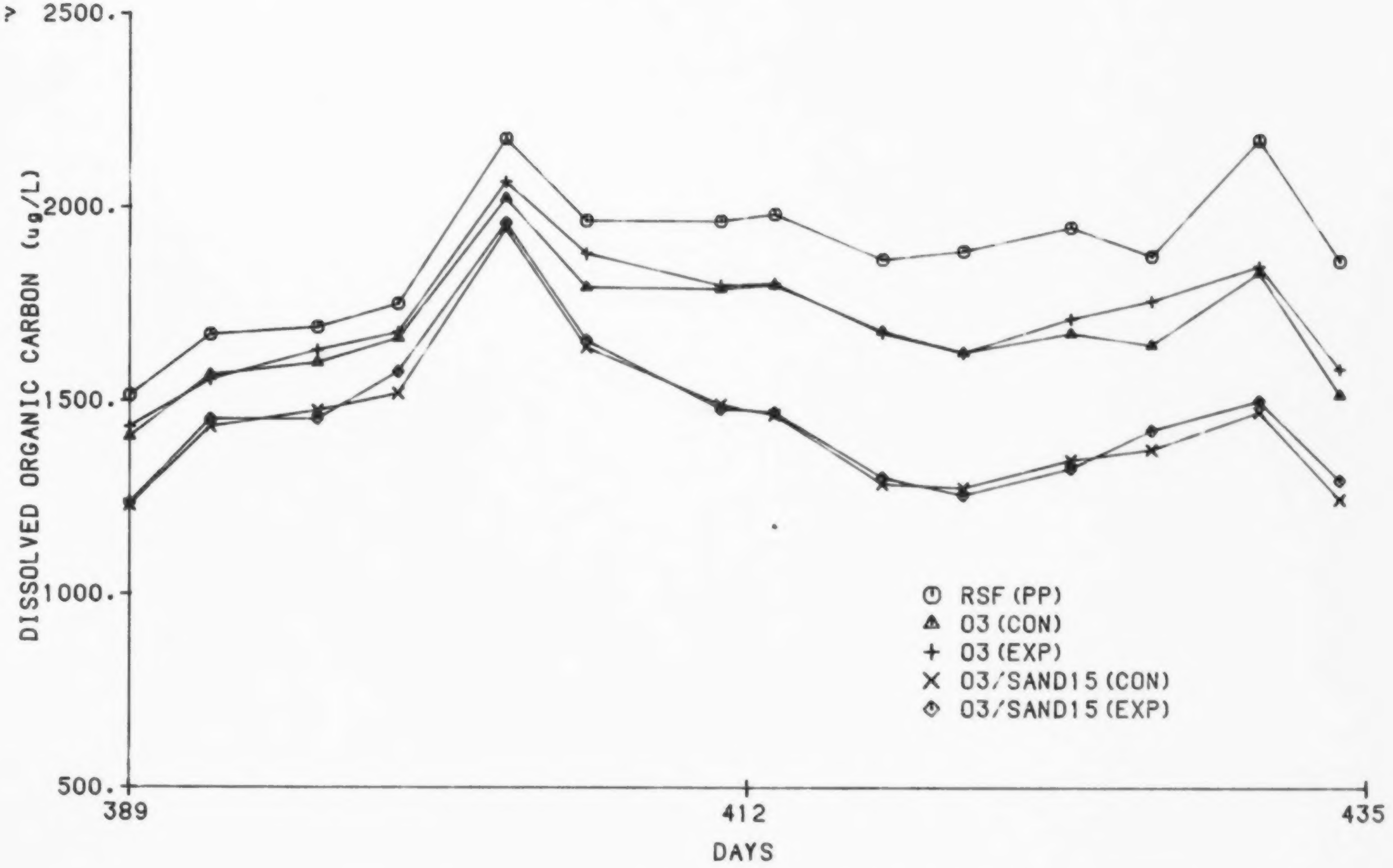

Figure 110. O_3/SAND Study #1 (Contactor Comparison): DOC results.

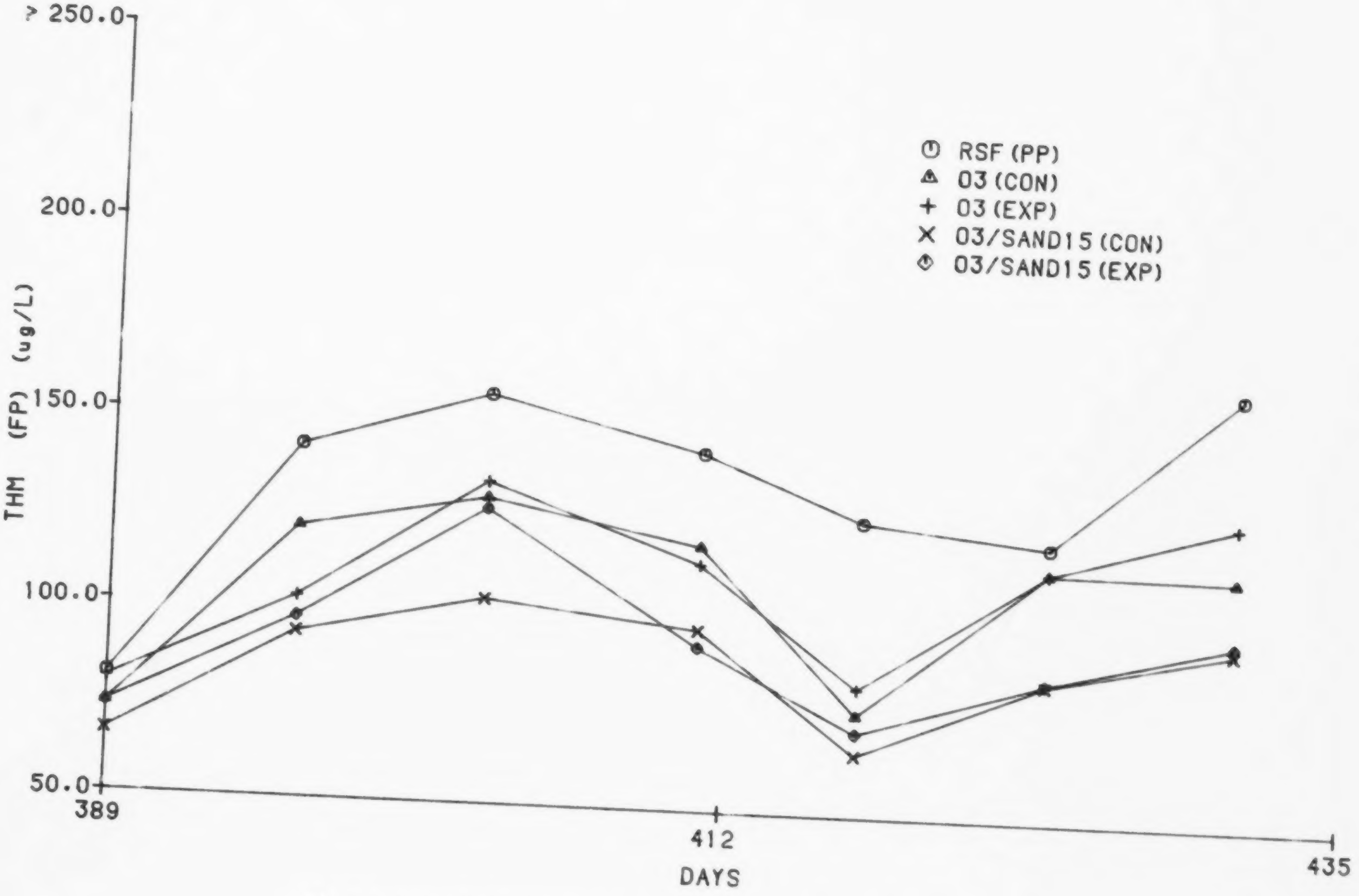

Figure 111. O_3/SAND Study #1 (Contactor Comparison): THMFP results.

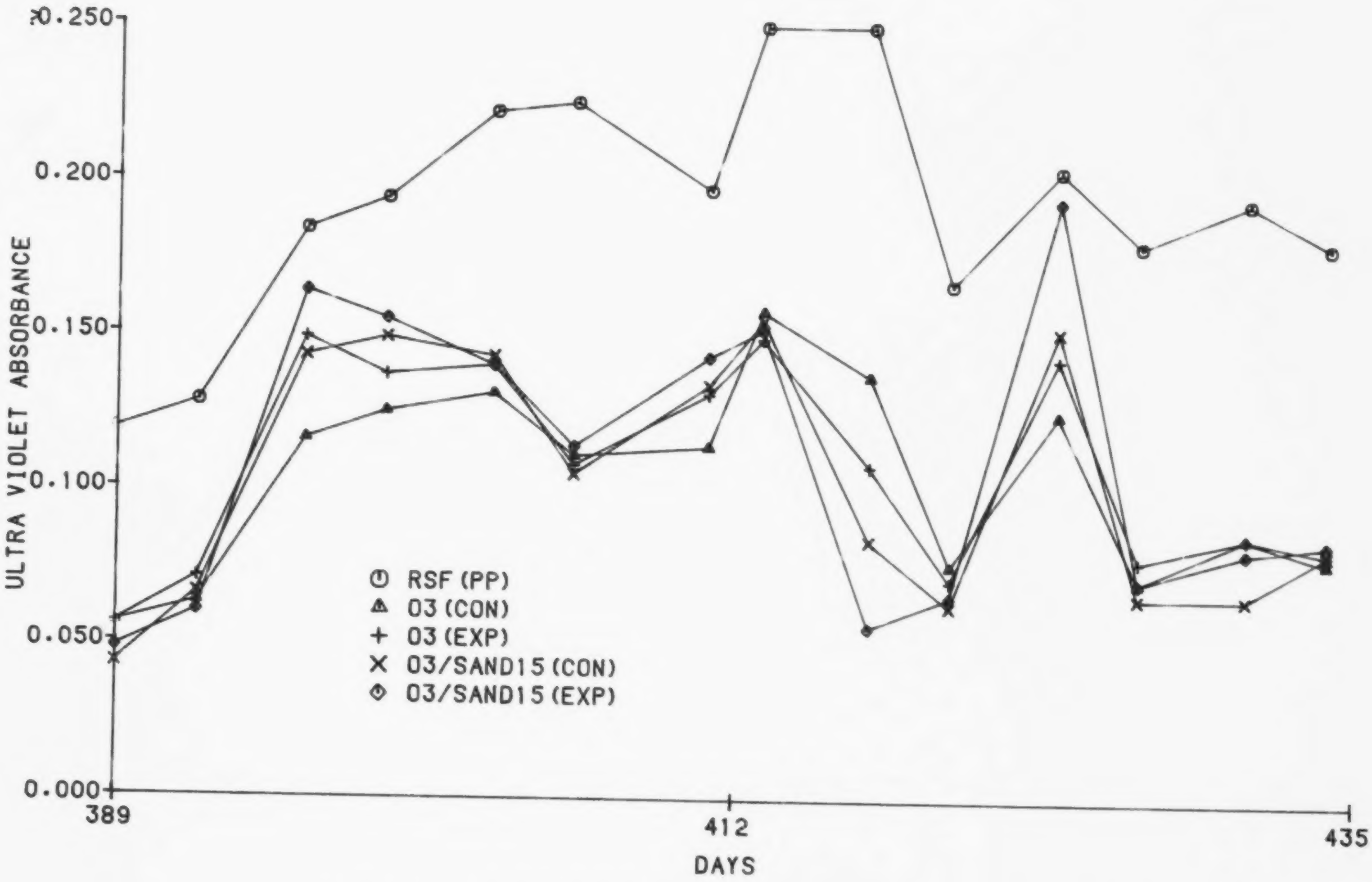

Figure 112. O_3/SAND Study #1 (Contactor Comparison): A254 results.

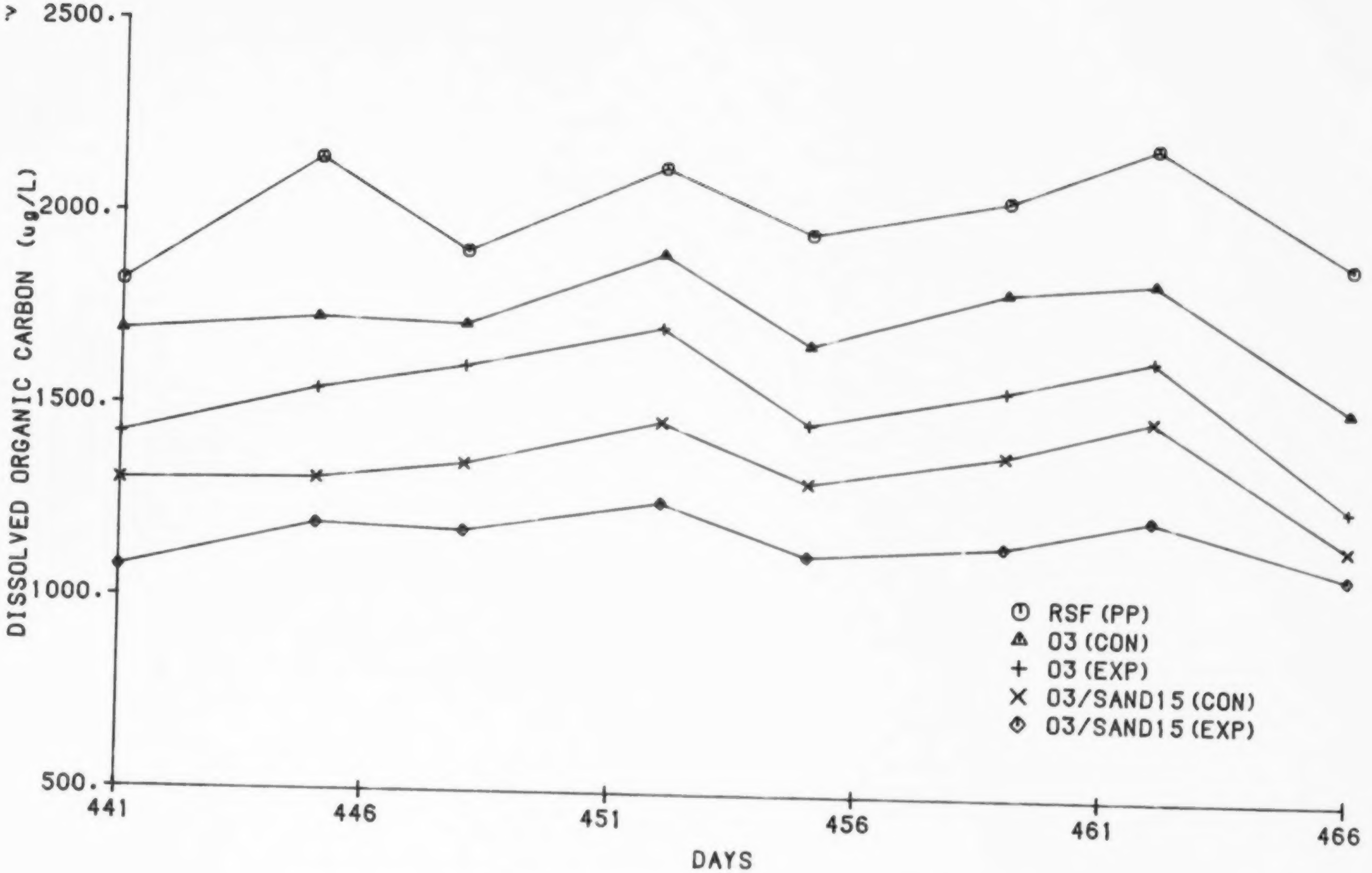

Figure 113. O_3/SAND Study #2 (Contact Time Comparison): DOC results.

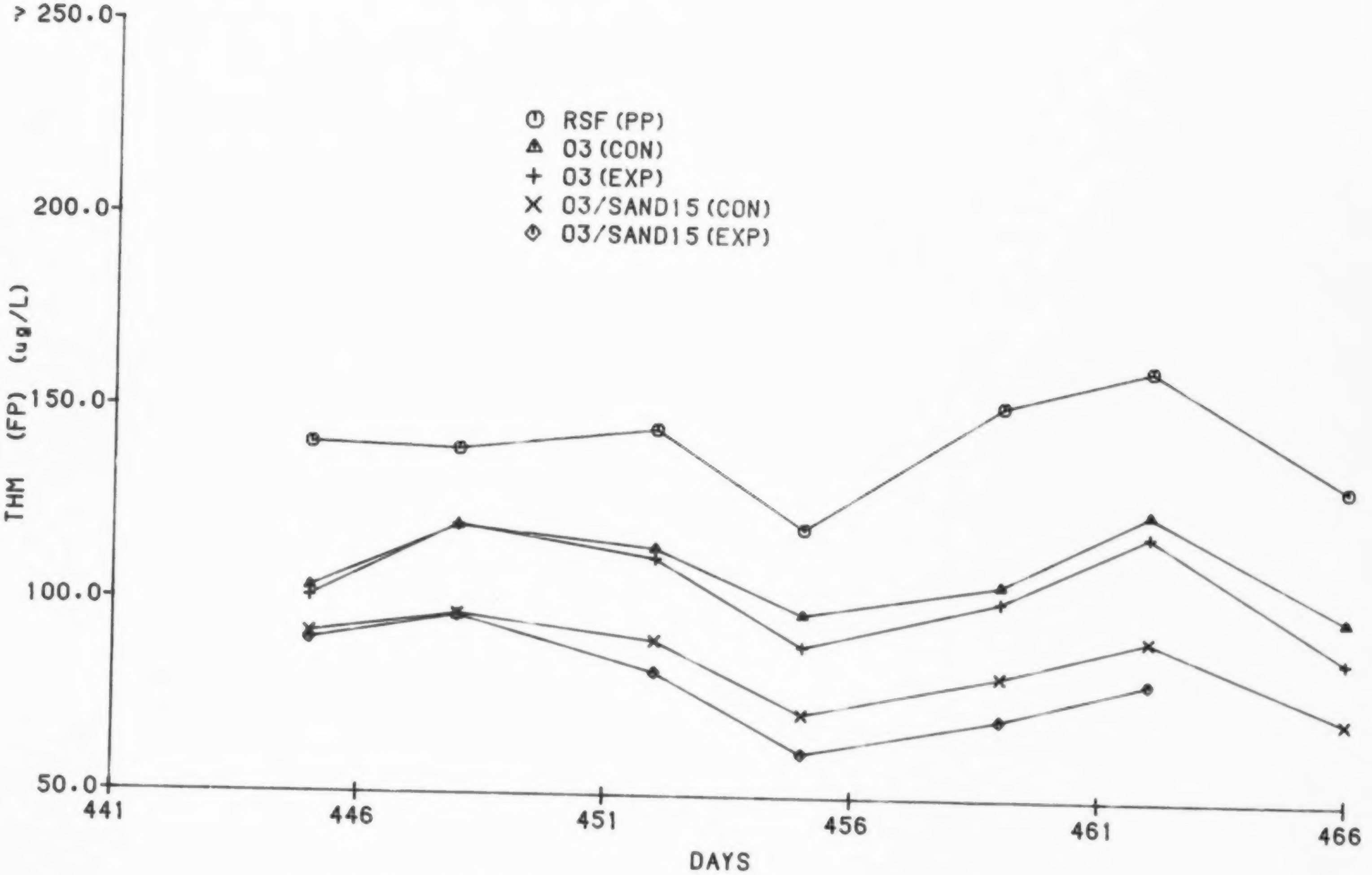

Figure 114. O_3/SAND Study #2 (Contact Time Comparison): THMFP results.

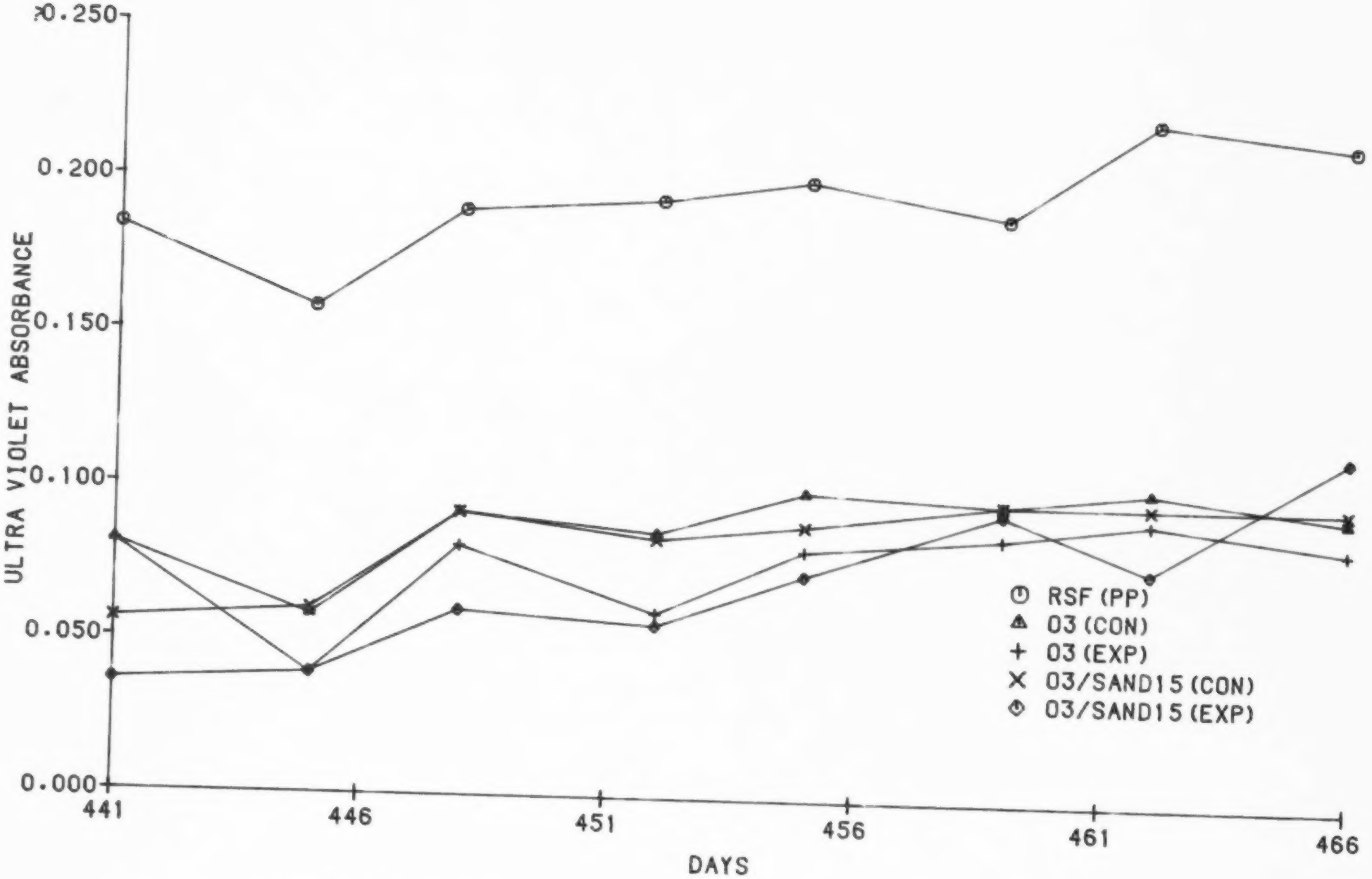

Figure 115. O_3/SAND Study #2 (Contact Time Comparison): A254 results.

the ozone dosage to the experimental ozone contactor was also doubled. The results of this investigation are summarized in Table 59 and are shown in Figures 116 to 118.

Compared with the results observed when contact time only was increased, a considerable improvement was observed when both contact time and ozone dosage were increased simultaneously. The improved performance for DOC removal was evident in both the ozone contactor and the sand bed; for THMFP, the operating changes resulted mostly in additional precursor biodegradability; for A254 absorbing compounds, changes were noted only in reductions through the ozone contactor itself.

Ozone Dosage Comparison--The objective of the fourth study was to determine whether the very positive results observed during the third ozone/sand study were due to additive or synergistic effects of the two altered operating parameters. These results are presented in Figures 119 to 121 and are summarized in Table 60. The results indicate that increased ozone dosage without simultaneous increases in ozone/water contact time results in little additional organic oxidation.

Cocurrent versus Countercurrent Flow--The final ozone/sand study measured the relative effectiveness of the cocurrent versus the countercurrent ozone contactor designs. The results of this study are presented graphically in Figures 122 to 124 and is summarized in Table 61. The results of this study showed that the direction of water flow had no significant effect upon the ability of the ozone system to oxidize organics.

Ozone Utilized--Figure 125 presents a plot of the ozone utilized by the two ozone contactors during the five ozone/sand studies. When operating conditions were identical (which apparently occurred during Study #5 as well as during Study #1), the standard deviation of the difference in ozone utilized between the two contactors was ± 0.53, well below the ± 1.03 standard deviation found for the lab-scale ozone utilized values (See Table 36). During the studies where ozone dose and/or contact time were increased, the ozone utilized by the experimental system was increased substantially when compared to the control system, indicating that the ozone utilized parameter responded to changes in operating conditions of the ozonation system.

Specific Organics--Although the sand systems showed no ability to remove volatile organics, changes in the ozone operating conditions offered an opportunity to investigate further the ozonation process. Table 62 shows the effect of contact time and ozone dose on the percent removal of several volatile organic compounds (chloroform, dichlorobromomethane, and 1,2-dichloropropane) from the ozone contactors. The data was compiled from grab samples which were collected three times per week. The results indicate that any increase in volatile organic removal was due to increased purging time and not due to any additional compound breakdown as a result of increased ozone dosage. Purging of these compounds was also not affected by a change in the direction of water flow through the contactor.

In addition, 1,2-dichloroethane and dibromochloromethane decreased by >25% on one occasion during the contact time experiment. During the contact

TABLE 59. O_3/SAND #3 (CONTACT TIME & DOSAGE COMPARISON)

PARAMETER	RSF	CONTROL SYSTEM				EXPERIMENTAL SYSTEM			
		OZONE CONTACTOR		SAND BED		OZONE CONTACTOR		SAND BED	
		Amount	%Δ	Amount	%Δ	Amount	%Δ	Amount	%Δ
DOC(ppb)	2059	1686	18.1	1336	35.1	1433	30.4	990	51.9
THMFP(ppb)	145	112	22.8	90	37.9	106	26.9	73	49.7
A254	0.166	0.068	59.0	0.059	64.5	0.054	67.5	0.047	71.7

OZONE	CONTROL SYSTEM	EXPERIMENTAL SYSTEM
-Dose(mg/1)	2.1	4.1
-Contact Time(min)	22	44
-Utilized(mg/1)	0.97	3.52

Study Period-8/4/81 to 9/18/81

Both systems use PP RSF Effluent as water source.

%Δ based on RSF effluent

TABLE 60. O_3/SAND STUDY #4 (DOSAGE COMPARISON)

PARAMETER	RSF	CONTROL SYSTEM				EXPERIMENTAL SYSTEM			
		OZONE CONTACTOR		SAND BED		OZONE CONTACTOR		SAND BED	
		Amount	%Δ	Amount	%Δ	Amount	%Δ	Amount	%Δ
DOC(ppb)	1941	1624	16.3	1226	36.8	1566	19.3	1224	36.9
THMFP(ppb)	119	97	18.5	77	35.3	93	21.8	76	36.1
A254	0.145	0.065	55.2	0.041	71.7	0.052	64.1	0.041	71.7

OZONE	CONTROL SYSTEM	EXPERIMENTAL SYSTEM
-Dose(mg/1)	2.2	4.0
-Contact Time(min)	22	22
-Utilized(mg/1)	1.14	3.42

Study Period-9/19/81 to 10/9/81

Both systems use PP RSF Effluent as water source.

%Δ based on RSF effluent

TABLE 61. O_3/SAND STUDY #5 (COCURRENT VS. COUNTERCURRENT)

PARAMETER	RSF	CONTROL SYSTEM				EXPERIMENTAL SYSTEM			
		OZONE CONTACTOR		SAND BED		OZONE CONTACTOR		SAND BED	
		Amount	%Δ	Amount	%Δ	Amount	%Δ	Amount	%Δ
DOC(ppb)	2097	1900	9.4	1522	27.4	1894	9.7	1497	28.6
THMFP(ppb)	159	136	14.5	114	28.3	135	15.1	114	28.3
A254	0.165	0.090	45.5	0.064	61.2	0.071	57.1	0.066	60.0
OZONE		CONTROL SYSTEM				EXPERIMENTAL SYSTEM			
-Dose(mg/1)		2.0				2.0			
-Contact Time(min)		22				22			
-Utilized(mg/1)		1.46				1.26			

Study Period-10/10/81 to 11/13/81

Both systems use PP RSF Effluent as water source.

%Δ based on RSF effluent

TABLE 62. VOLATILE ORGANIC REMOVAL[a] FOR O_3/SAND STUDIES

OZONATION CONDITIONS					PERCENT REMOVALS					
					Chloroform		Dichlorobromomethane		1,2-Dichloropropane	
Study Number	Control (CT)	Control (Dose)	Experimental (CT)	Experimental (Dose)	Control Ozonator	Experimental Ozonator	Control Ozonator	Experimental Ozonator	Control Ozonator	Expermental Ozonator
1	22	1.2	22	1.2	36	31	35	32	36	37
2	22	1.5	44	1.5	45	59	43	59	48	67
3	22	2.1	44	4.1	42	55	37	50	52	67
4	22	2.2	22	4.0	27	28	21	23	58	60
5[b]	22	2.0	22	2.0	37	37	36	32	46	48

(CT) Contact Time - minutes

[a] % Removals from RSF effluent

[b] Countercurrent operation

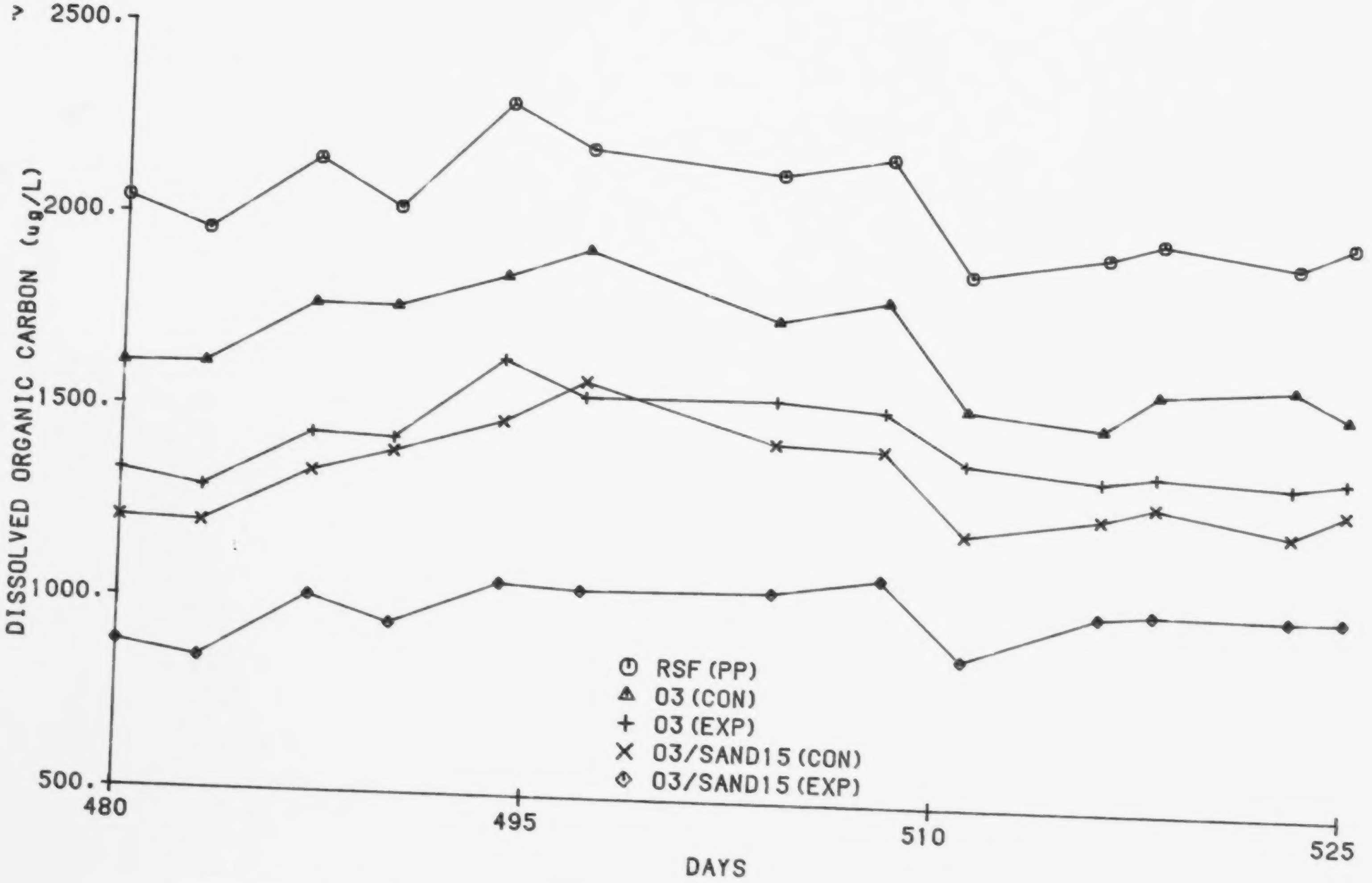

Figure 116. O_3/SAND Study #3 (Contact Time and Dosage Comparison): DOC results.

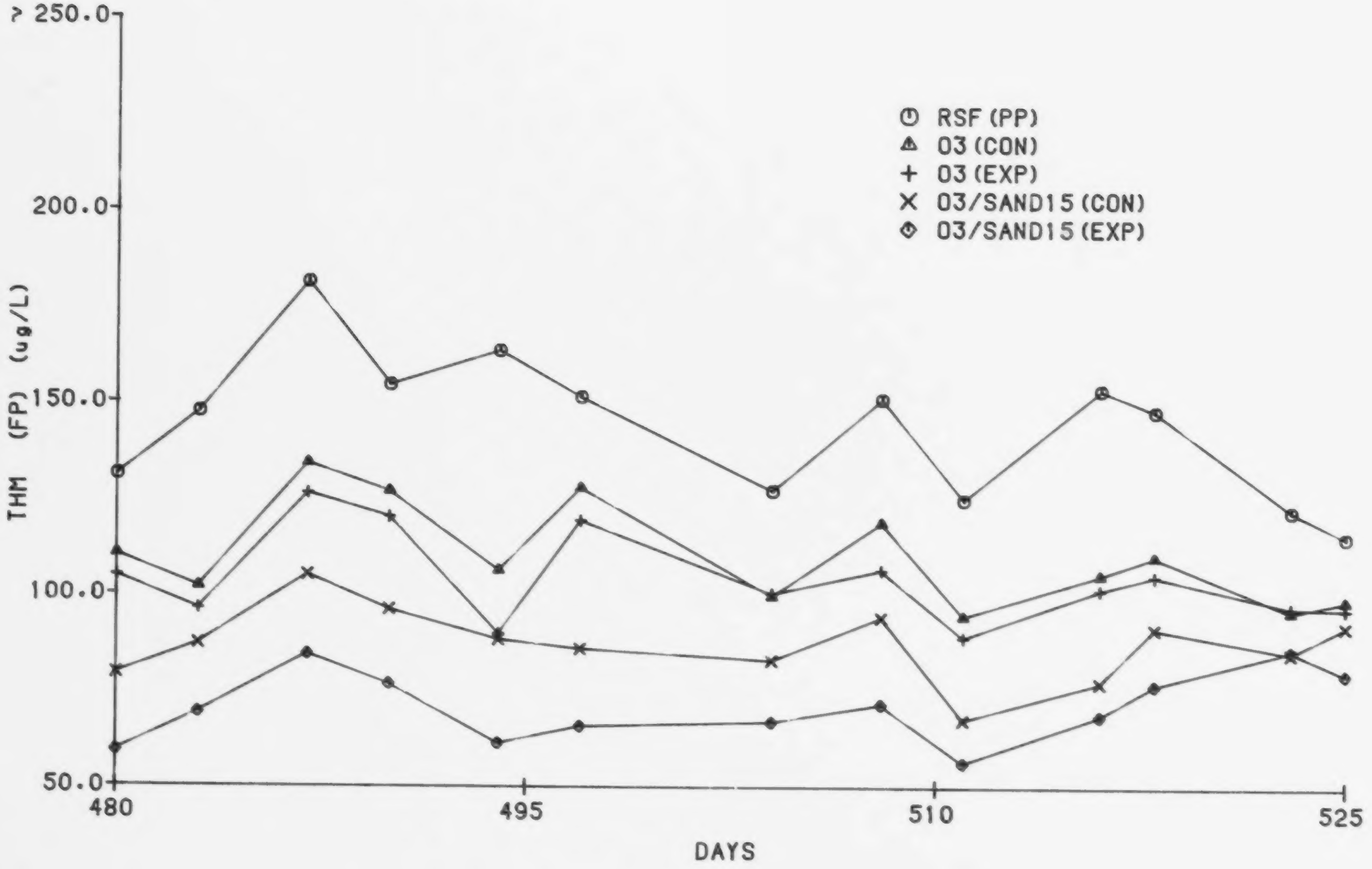

Figure 117. O_3/SAND Study #3 (Contact Time and Dosage Comparison): THMFP results.

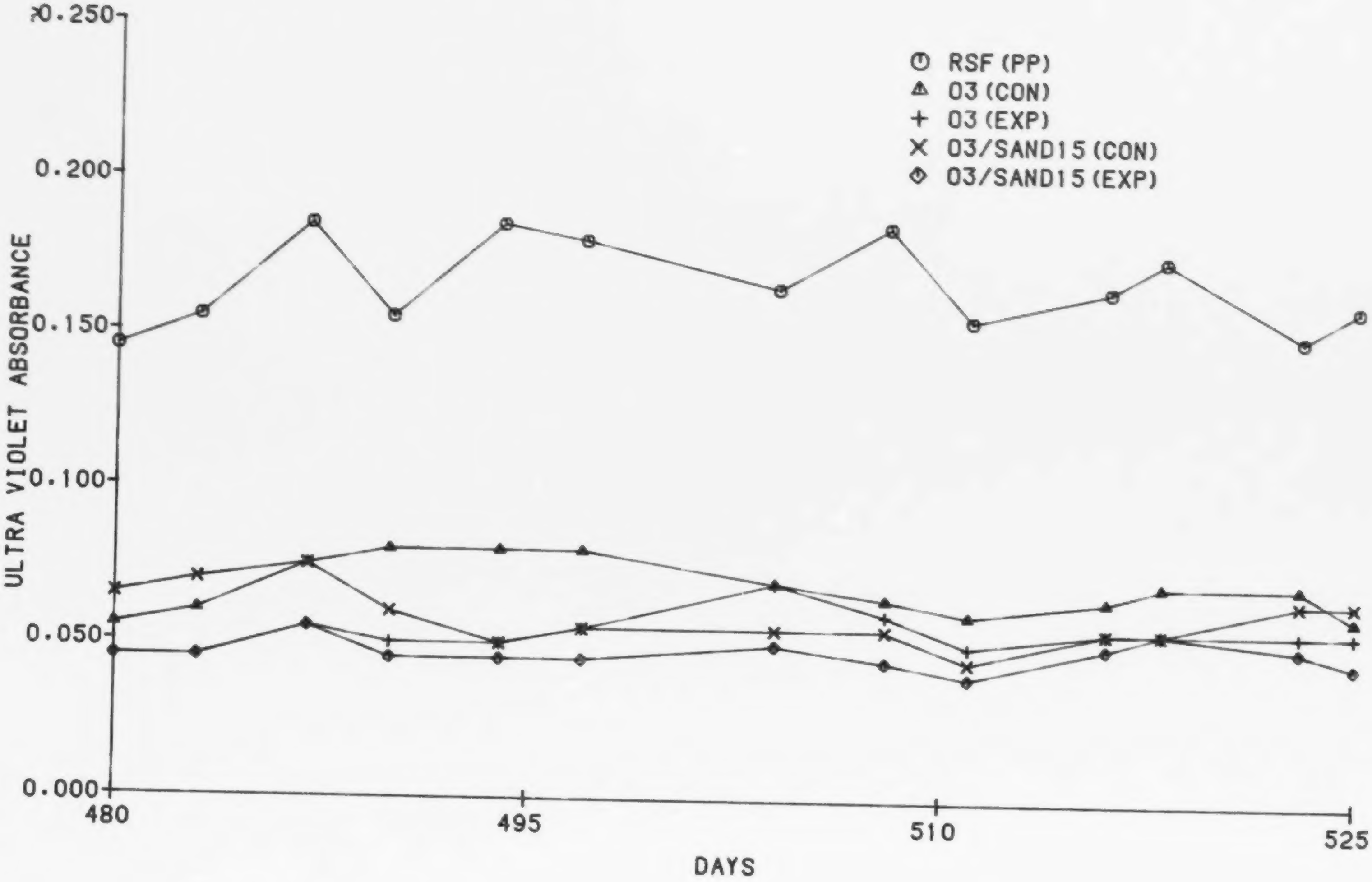

Figure 118. O_3/SAND Study #3 (Contact Time and Dosage Comparison): A254 results.

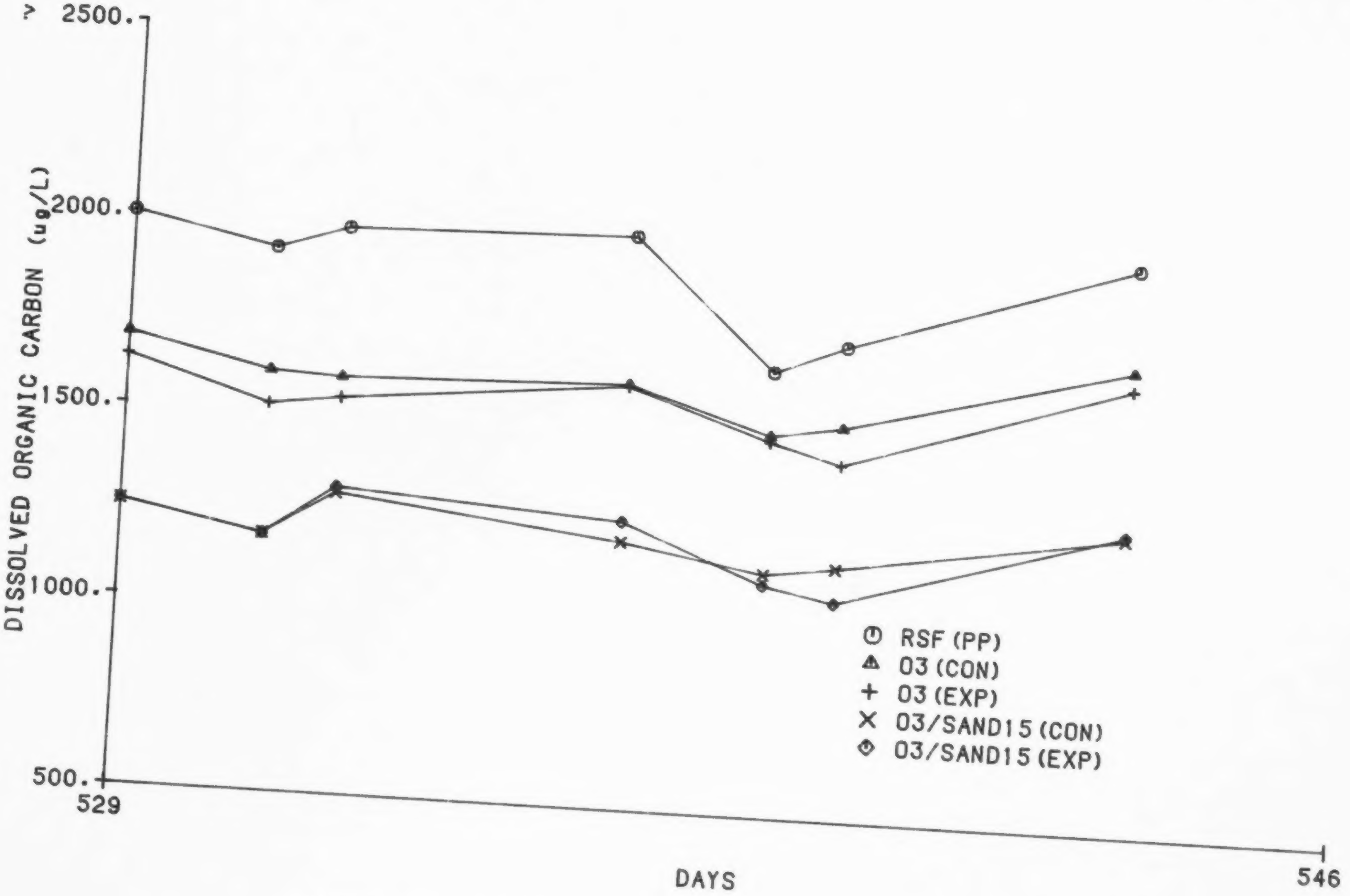

Figure 119. O_3/SAND Study #4 (Dosage Comparison): DOC results.

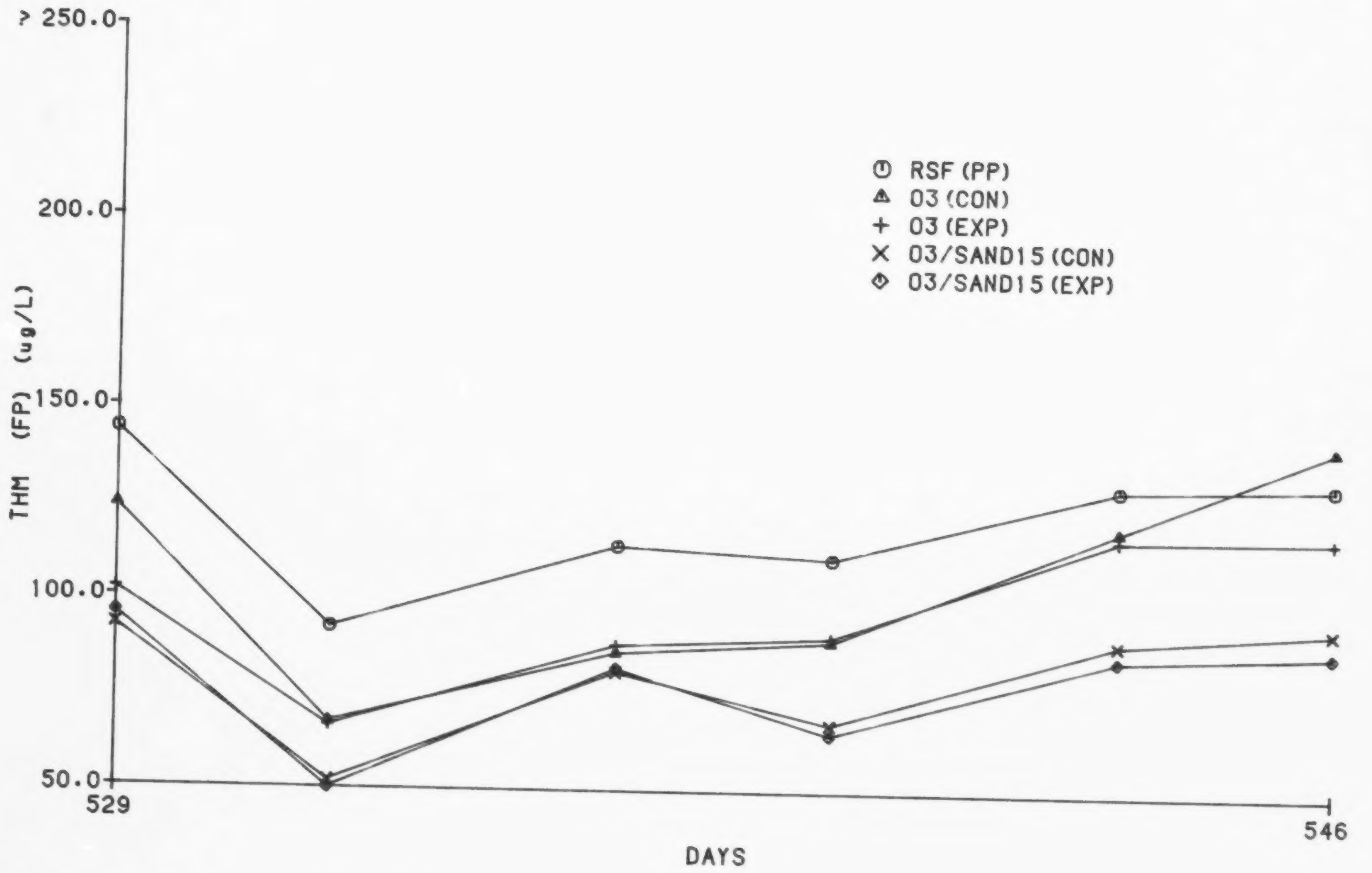

Figure 120. O_3/SAND Study #4 (Dosage Comparison): THMFP results.

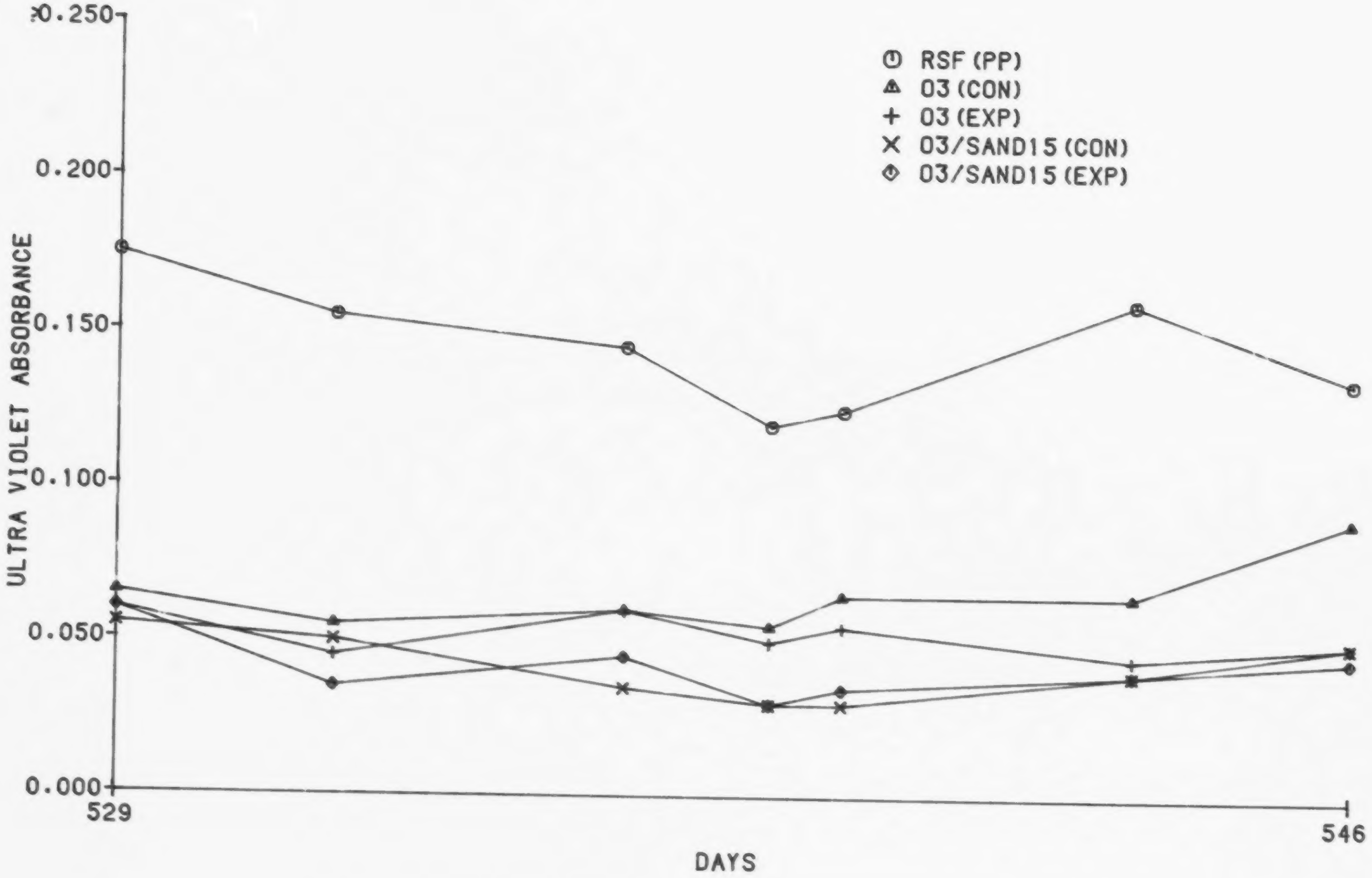

Figure 121. O_3/SAND Study #4 (Dosage Comparison): A254 results.

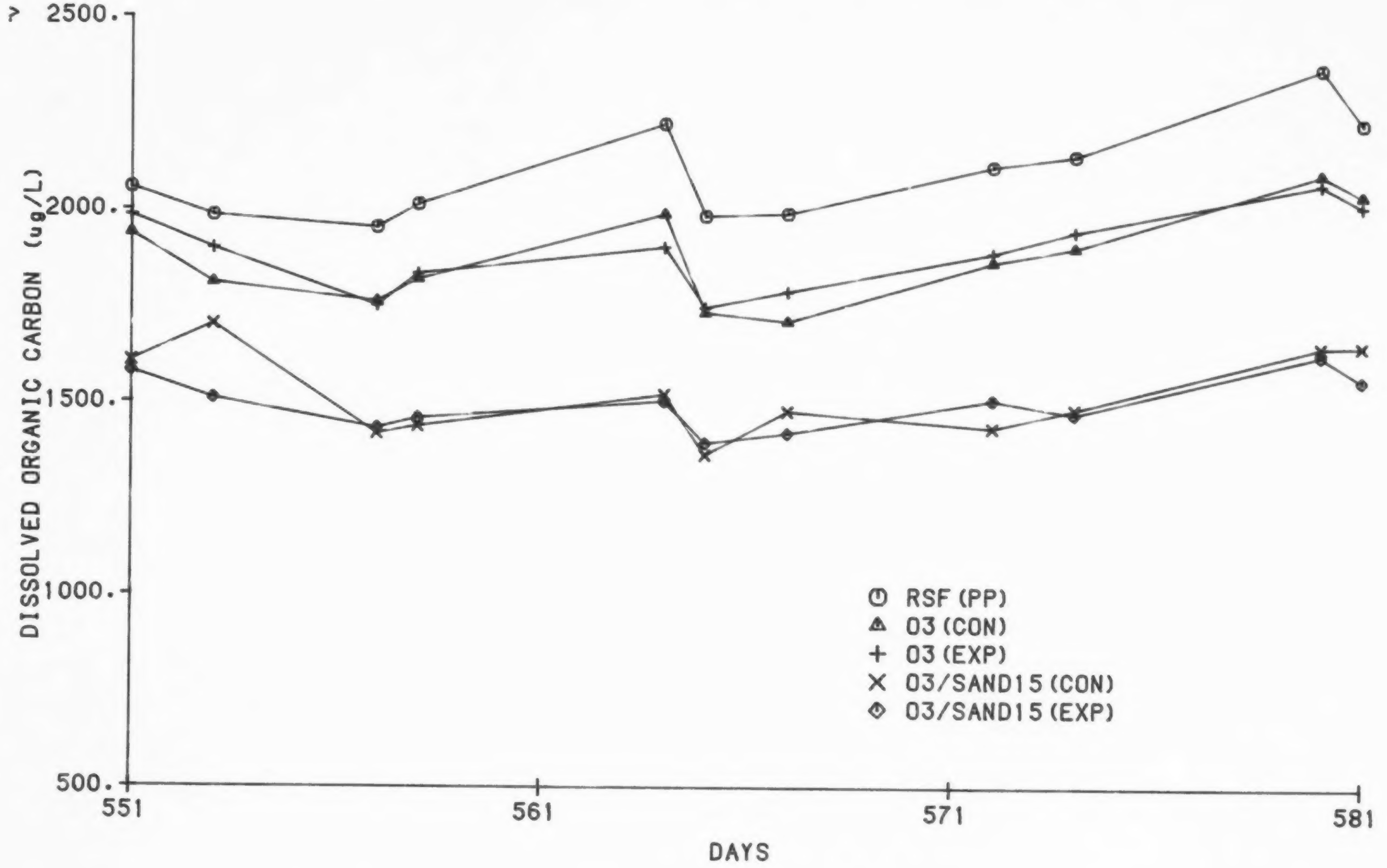

Figure 122. O_3/SAND Study #5 (Flow Direction Comparison): DOC results.

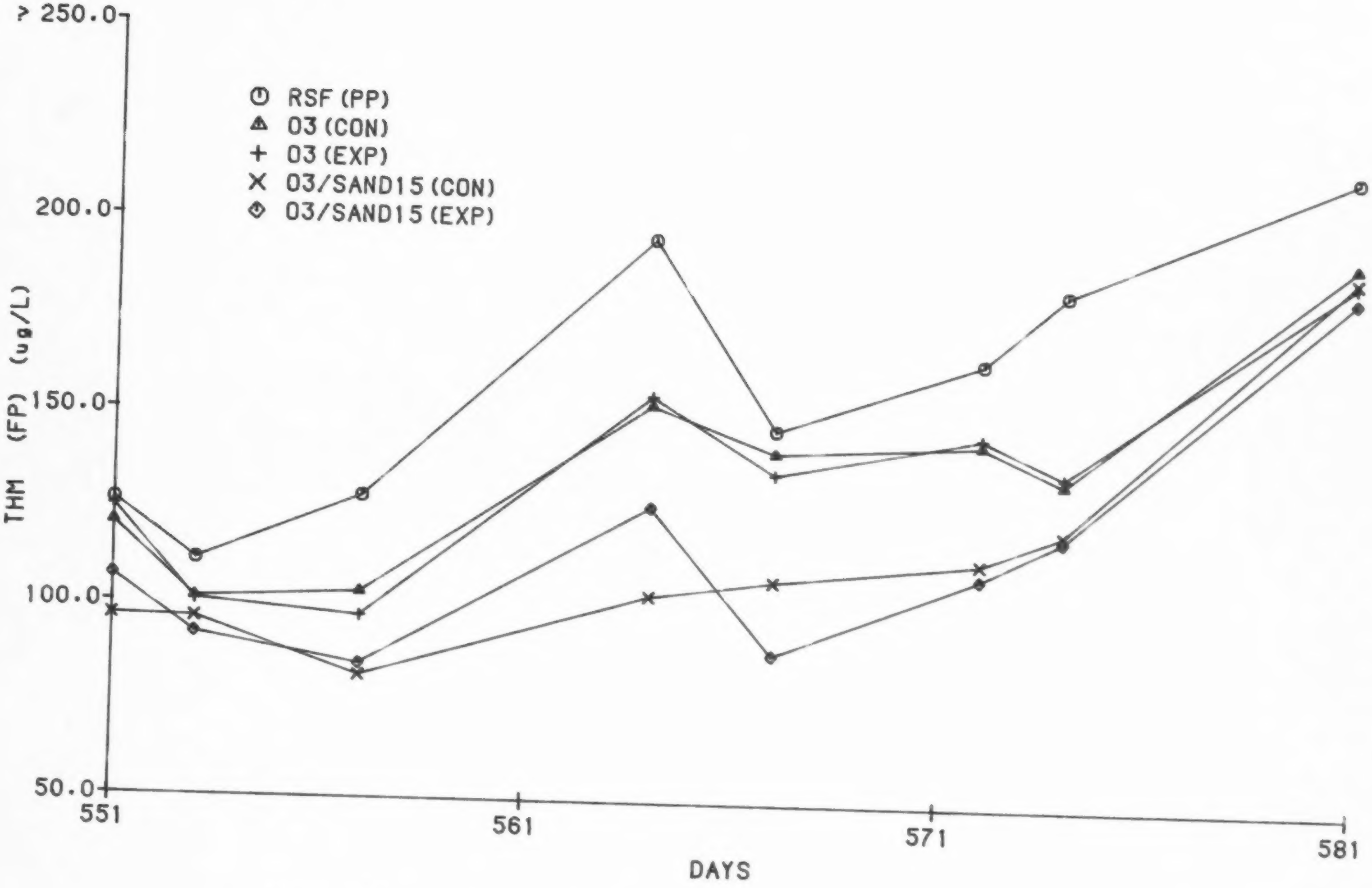

Figure 123. O_3/SAND Study #5 (Flow Direction Comparison): THMFP results.

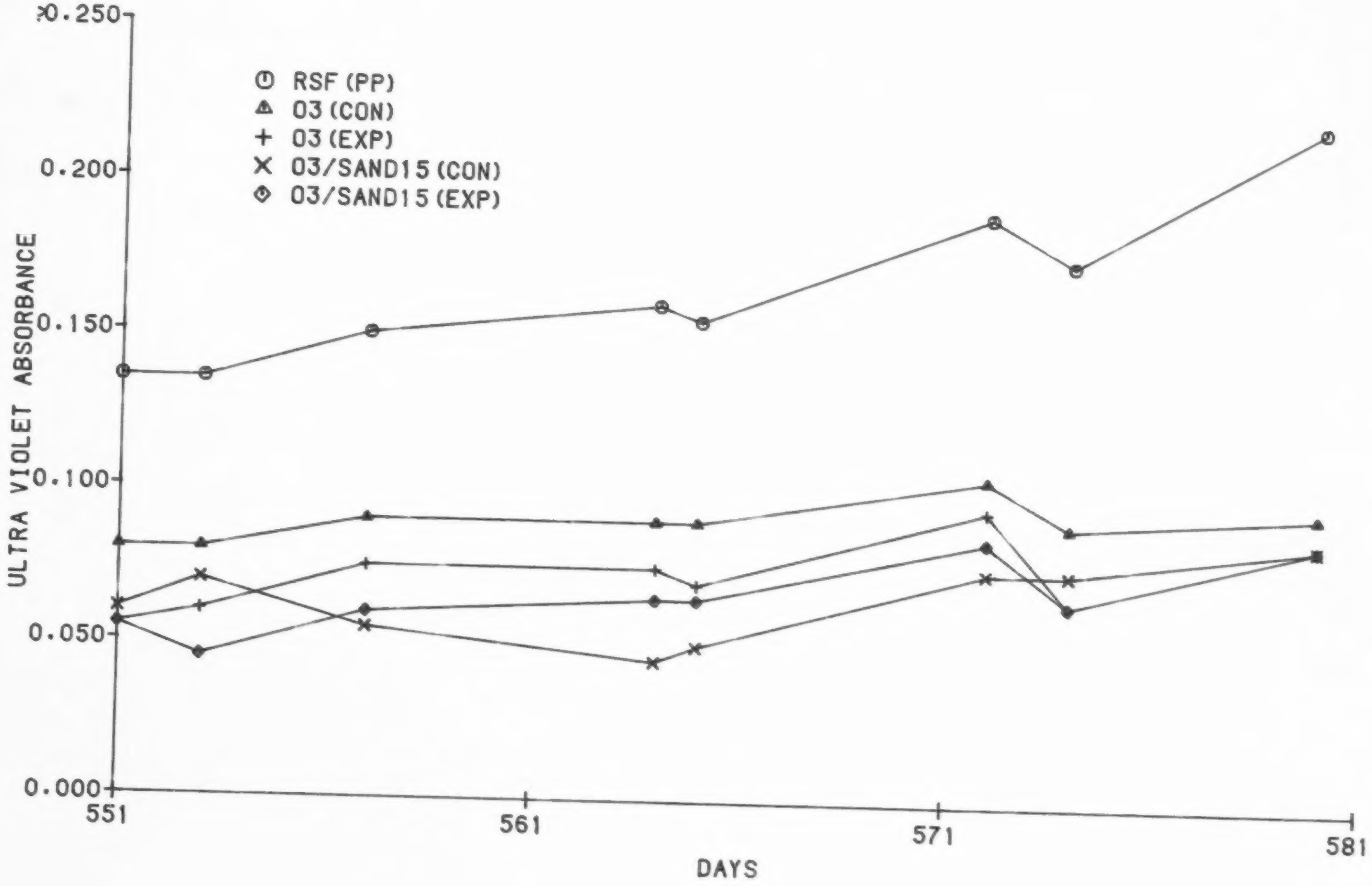

Figure 124. O_3/SAND Study #6 (Flow Direction Comparison): A254 results.

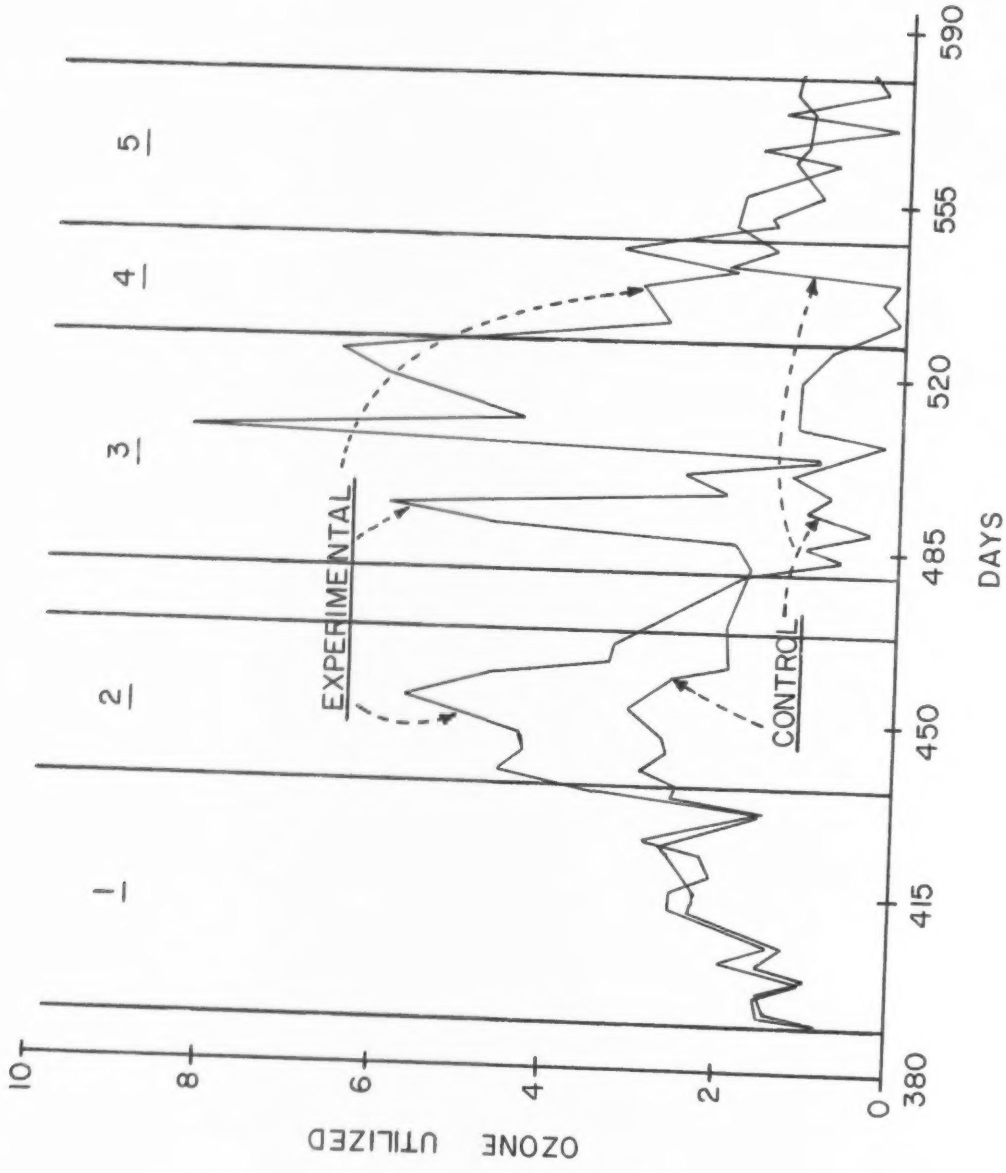

Figure 125. Comparison of ozone utilized values during O_3/SAND Studies.

time and dose experiment dibromochloromethane and bromoform showed >25% decrease for all samples analyzed while 1,2-DCE decreased >25% one time. Further analysis of the chromatographic data showed that with increased contact time, or contact time and dose, the acetone concentrations increased greater than 25% during five sampling periods. This was expected as acetone was observed to increase during ozonation (see Tables 42 and 46). During two different sampling periods, toluene (increase contact time) and benzene (increased contact time and dose) showed an increased concentration of greater than 25%. Benzene and toluene have previously been shown to increase during studies of ozonation of sewage (168). Two unidentified peaks at RRT 11.09 (increased contact time and dose) and 11.38 (increased contact time) also increased by greater than 25% in most samples. These peaks have not been idenified by GC/MS.

Microbiology Studies at the Pilot Plant

Enumeration and Identification of Total Coliforms --

Coliform densities isolated in the five treatment trains were examined in this study. Coliforms isolated from these trains were also identified. Total coliforms densities in the source water averaged 48,000/100ml. The Torresdale pretreatment process effectively removed 99% of the total coliforms from the source water. Only six coliforms were isolated during the study from the Torresdale treatment trains. Klebsiella pneumoniae was isolated from the Torresdale Filter effluent and five coliforms which were not identified were isolated at the beginning of the study from the ozonated GAC multi-tap column effluent. No coliforms were found in any other carbon column effluent using Torresdale treated water.

The Pilot Plant pretreatment process was not as effective as the Torresdale pretreatment process in the removal of coliforms. Coliforms were consistently isolated from the Pilot Plant Filter effluent and the effluent of GAC_{30}(PP). Coliforms were also occasionally isolated from effluents of the ozonator and the sand columns. Klebsiella pneumoniae and Enterobacter cloacae were the most common organisms isolated at these locations. Table 63 lists the locations where coliforms were isolated in both treatment systems, the total number found and their identification.

Enumeration and Identification of (AFAH) Bacteria --

AFAH bacterial densities at key locations in the five advanced water treatment trains were followed throughout this study (Table 64). Moreover, dominant organisms at these locations were identified and patterns in species succession recorded. Total bacterial counts in the Delaware River source water ranged from a low of 5,300/ml in January to a high of 146,000/ml in October. The Torresdale pretreatment process effectively reduced these counts to approximately 40/ml. Ozonation further reduced this level to <10 bacteria/ml.

Water from the ozone retention tank flowed simultaneously into two GAC columns ($GAC_{15,30}$(TP)), two Ozone-GAC columns ($O_3/GAC_{15,30}$(TP)), and a small multitap ozone GAC column (MT_{15}). Average bacterial counts in the influent and effluents of the GAC columns are represented in Figure 126. Bacterial densities in the effluents of the Torresdale GAC columns were 100 to 1000

TABLE 63. COLIFORM BACTERIA ISOLATED FROM THE TORRESDALE AND PILOT PLANT TREATMENT TRAINS FROM 4/16/80 TO 4/13/81

Location	Total Number of Organisms Isolated	Identification*
RSF (TP)	1	*Kl. pneumoniae*
MT$_{15}$ (TP)	5	None
RSF (PP)	146	76 *A. hydrophilia* 22 *Kl. oxytoca* 21 *C. freundii* 15 *Kl. pneumoniae* 10 *Ent. agglomerans* 2 *Ent. sakazakie*
O$_3$RT (PP)	7	1 *Kl. oxytoca* 4 *Ent. cloacae* 2 *E. coli*
O$_3$/GAC$_{30}$ (PP)	7	2 *A. hydrophilia* 5 *Kl. oxytoca*
O$_3$/SAND$_{30}$ (PP)	5	2 *C. freundii* 3 *Ent. cloacae*
GAC$_{30}$ (PP)	75	59 *A. Hydrophilia* 13 *C. freundii* 2 *Ent. cloacae* 1 *Kl. oxytoca*
MT$_{15}$ (PP)	3	2 *Ent. cloacae* 1 *Past. multocida*(?)

* A. = *Aeromonas*, C. = *Citrobacter*, E. = *Escherichia*, Ent. = *Enterobacter*, Kl. = *Klebsiella*, Past. = *Pasteurella*

(PP) = Pilot Plant

(TP) = Torresdale Plant

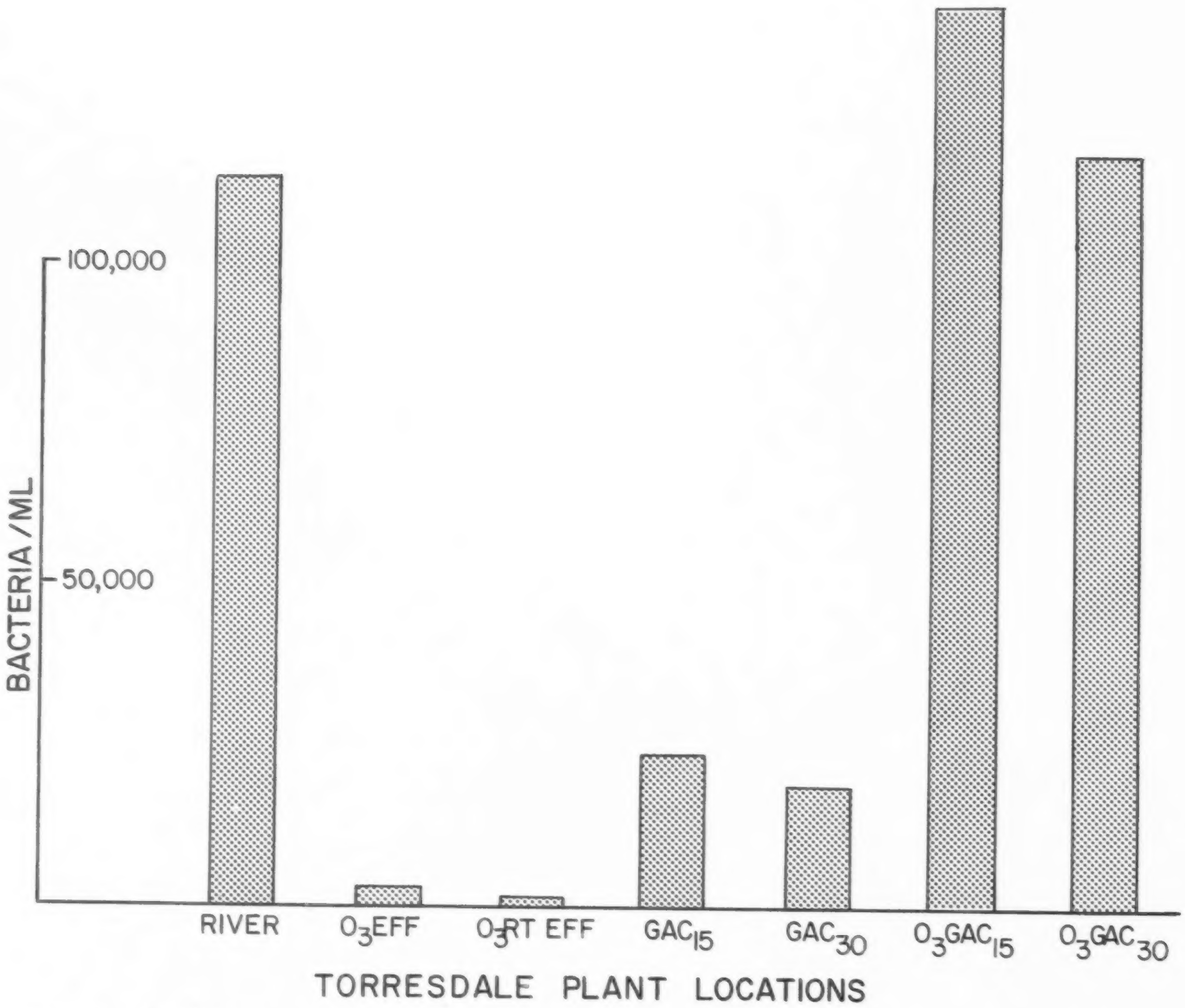

Figure 126. Average number of heterotrophic bacteria through the Torresdale Plant.

times greater than that of the influent. As can be seen in Figures 127 and 128, the density of bacteria in both the ozonated and non-ozonated carbon columns increased rapidly to 10^5-10^6 bacteria/ml and then leveled off at 10^4 bacteria/ml for the rest of the study.

Seventy dominant bacteria isolated from the above locations were identified and can be found in Table 64. The predominant bacteria in the river included 14 species of *Pseudomonas*, 3 species of *Alcaligenes*, 5 species of *Flavobacterium*, 2 species of *Acinetobacter*, 1 species of *Azotobacter*, *Achromobacter* and *Cytophoga* and several unidentified species of *Bacillus* and *Micrococcus*. Chlorination and ozonation successfully destroyed most of this mixed population with the exception of *Bacillus* and *Flavobacterium*. However, once the remaining bacteria entered the GAC columns and the bactericidal effects of the oxidants were destroyed by reduction of the activated carbon itself, the bacterial density increased. The bacterial community found in the effluents of the ozonated and nonozonated carbon columns were basically the same. *Pseudomonas* and *Flavobacterium*, were the predominant organisms throughout the year. Major changes in the species composition of these populations occurred in the spring and fall and were therefore thought to be temperature related. As can be seen in Figures 129 & 130, *Acinetobacter* and *Alcaligenes sp*. appeared in greater numbers in early Spring when the water temperature exceeded 10°C whereas *Bacillus* was found in greater numbers in early autumn when water temperatures were at their peak. As will be shown later, chlorine effectively eliminated 99.9% of these bacteria.

Pretreatment unit processes in the Pilot Plant (non-disinfected) did not eliminate bacteria as effectively as the Torresdale system (chlorinated). Figure 131 represents the average counts of bacteria at specified locations in the Pilot Plant system. Bacteria counts in the influent to the ozonator averaged 13,000/ml. This nonozonated water served as the influent to GAC_{15} (PP). Ozone inactivated 98% of these bacteria. However, bacterial growth was found to occur in the ozone retention tank so that influent waters to the ozone/GAC and ozone/sand columns contained approximately 900 bacteria/ml. Bacteria counts in the effluents of the ozonated Pilot Plant carbon columns $(O_3/GAC_{15,30})$ leveled off at 10^4/ml. Bacteria counts in the sand column effluents of the Pilot Plant $(O_3/Sand_{15,30})$ leveled off at slightly higher levels of 10^4 to 10^5/ml. However, bacterial counts in the nonozonated carbon column effluents, $(GAC_{15,30})$ which had 15 times more bacteria in its influent waters, leveled off at 10^2 to 10^3 bacteria/ml. The plots in Figures 132 to 135 present the bacterial counts in the effluents of these Pilot Plant carbon and sand columns throughout the study.

The bacterial populations in the ozonated columns were also examined. Figure 136 presents the bacterial counts in two ozonated GAC columns. As can be seen, counts for both columns reached 10^8 per ml in the first two weeks and remained there throughout the study. Average bacterial counts in the O_3/GAC_{15} (TP) column and its effluent were consistently higher then those of the O_3/GAC_{15} (PP) column even though influent bacterial levels of the O_3/GAC_{15} (PP) column were approximately 100 times greater than those in the influent of the O_3/GAC_{15} (TP) column.

Eighty-seven predominant bacteria were isolated from the Pilot Plant

TABLE 64. BACTERIA ISOLATED FROM THE TORRESDALE & PILOT PLANT TREATMENT TRAINS

- *Pseudomonas*
  - *Ps. aeuruginosa*
  - *Ps. cepacia*
  - *Ps. putida*
  - *Ps. acidovorans*
    - VA-1
    - VA-2
  - *Ps. alcaligenes*
  - *Ps. visiculare*
  - *Ps. pseudoalcaligenes*
  - *Ps. testosteroni*
  - *Ps. fluorescens*
  - *Ps. diminuta*
  - *Ps. putrefaciens*
  - *Ps. stutzeri*
- *Alcaligenes*
  - *Alcalegenes denitrificans*
  - *Alcaligenes odorans*
  - *Alcaligenes faecalis*
- *Aeromonas hydrophila*
- *Bacillus*
- *Achromobacter*
- *Cytophaga*
- *Acinetobacter*
  - *Acinetobacter lwoffi*
  - *Acinetobacter anitratum*
- *Azobacter*
- *Micrococcus*
- *Flavobacterium Species*
  - *Flavobacterium*
  - II J
  - II K-1
  - II B
  - II F
- *Arthrobacter*

AFAH - Aerobic and Facultative anaerobic heterotrophic (bacteria) recovered from both the Standard Plate Count and Soil Extract Agar Plate Count Procedure (See Experimental Section).

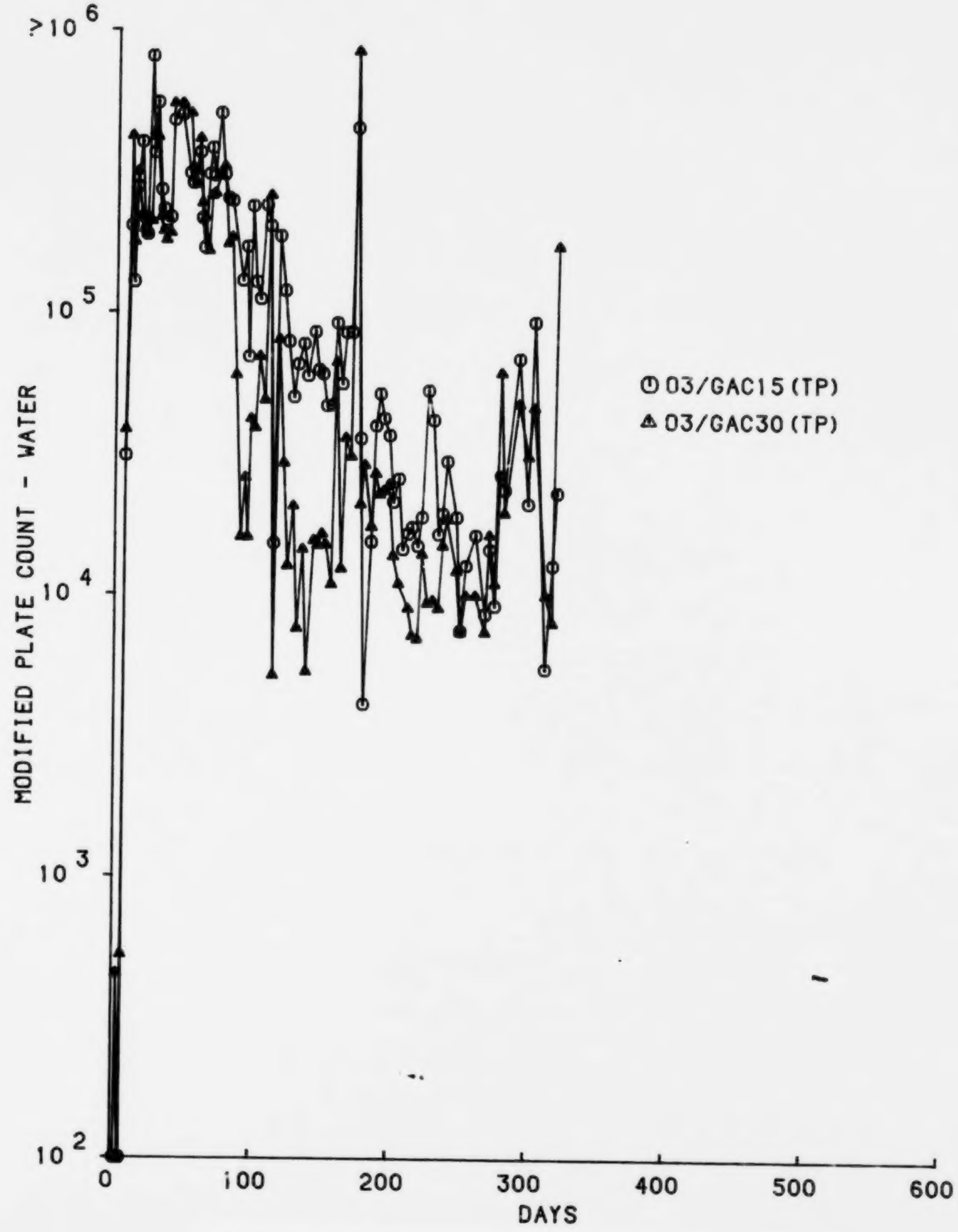

Figure 127. Heterotrophic bacterial levels in the Torresdale Plant O_3/GAC system effluents.

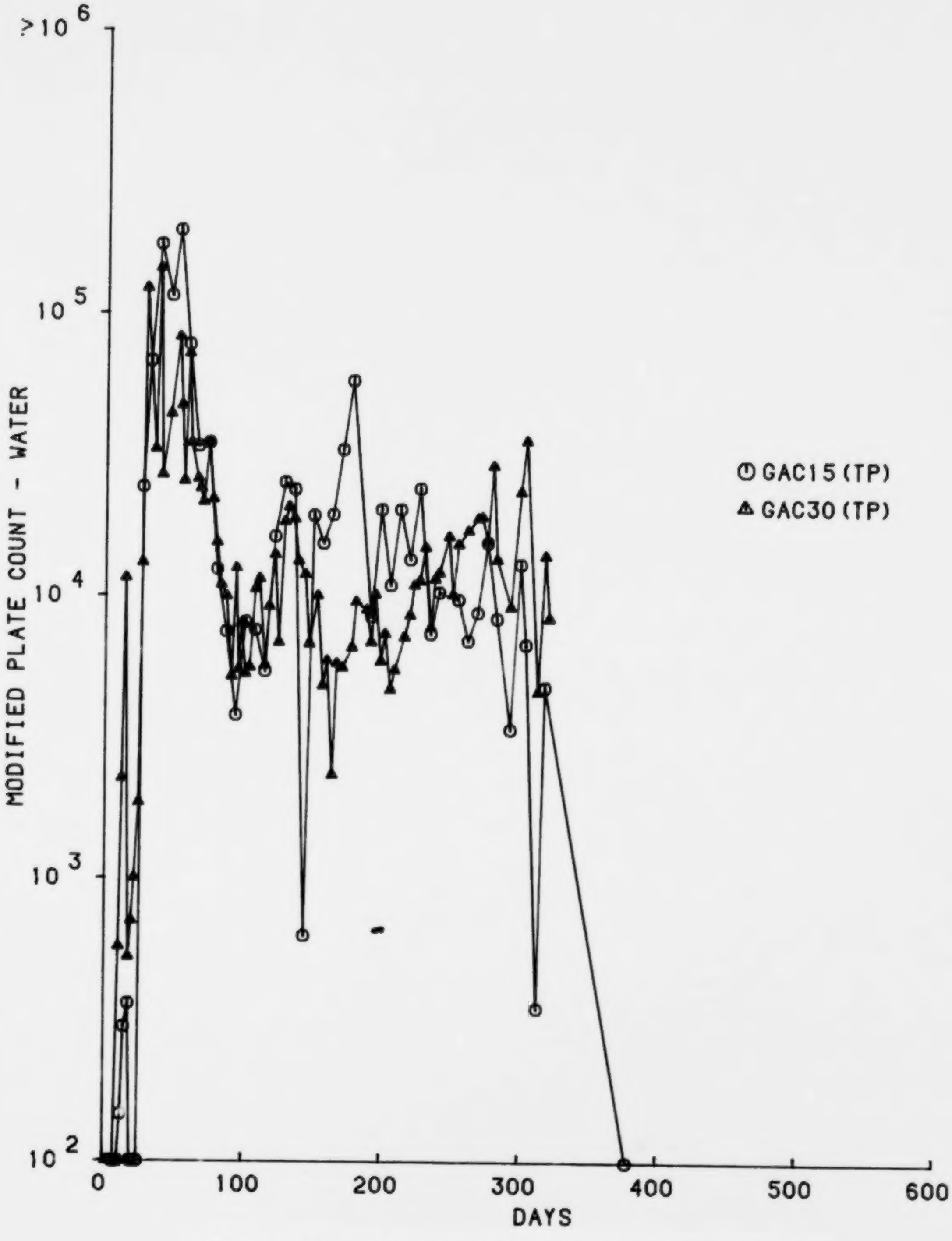

Figure 128. Heterotrophic bacterial levels in the Torresdale Plant GAC system effluents.

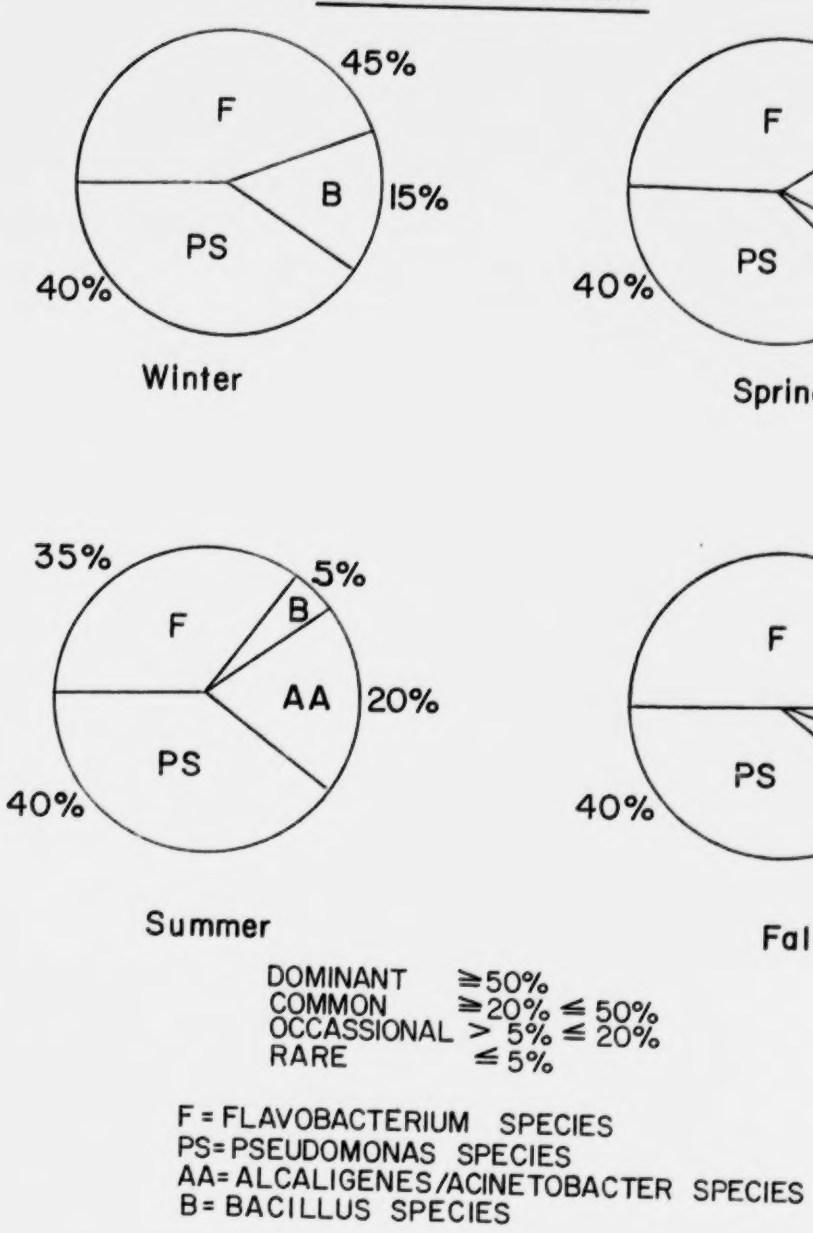

Figure 129. The composition of heterotrophic bacteria isolated from the Delaware River (4/80 to 3/81).

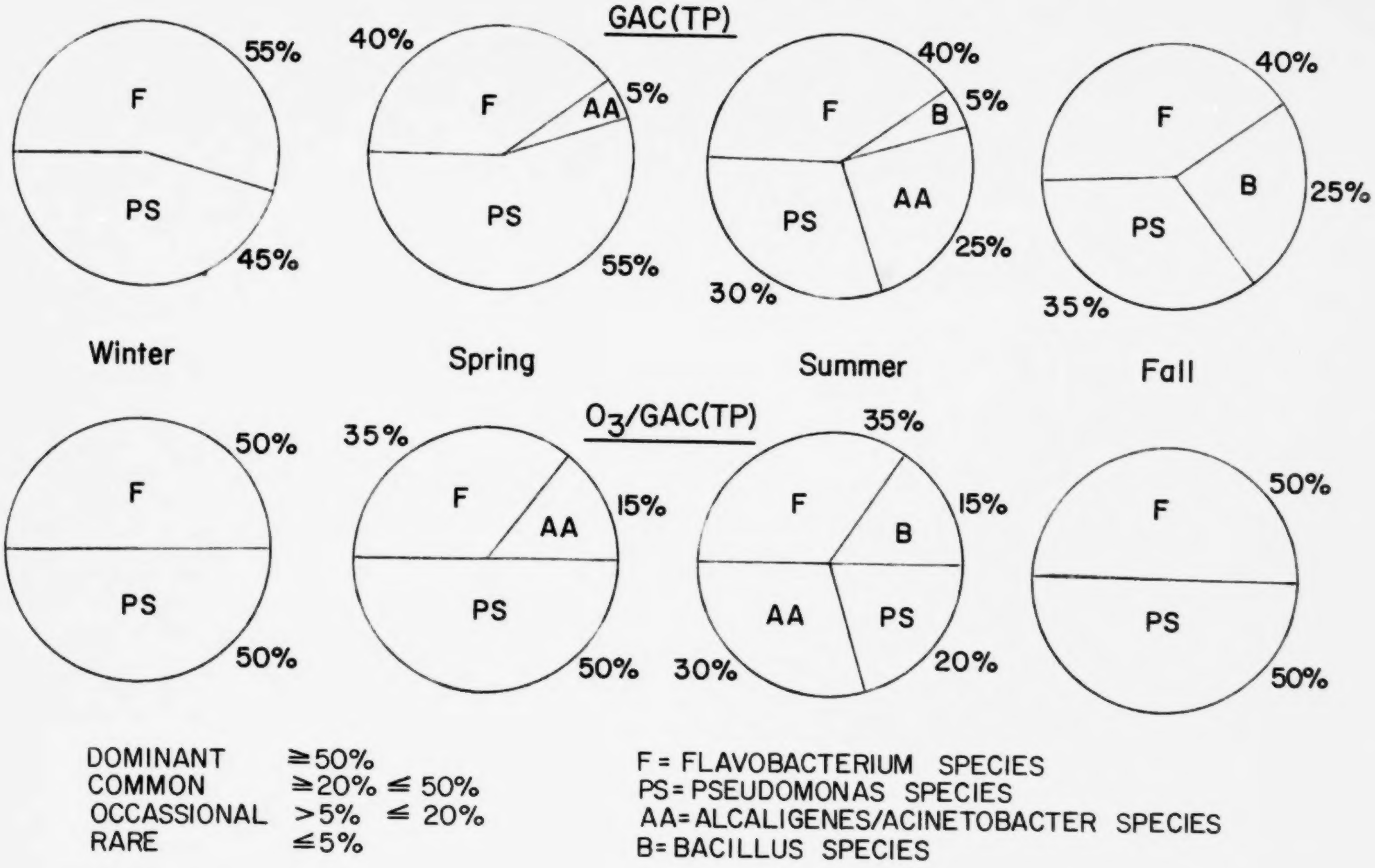

Figure 130. The composition of heterotrophic bacteria isolated in the Torresdale adsorption system effluents (4/80 to 3/81).

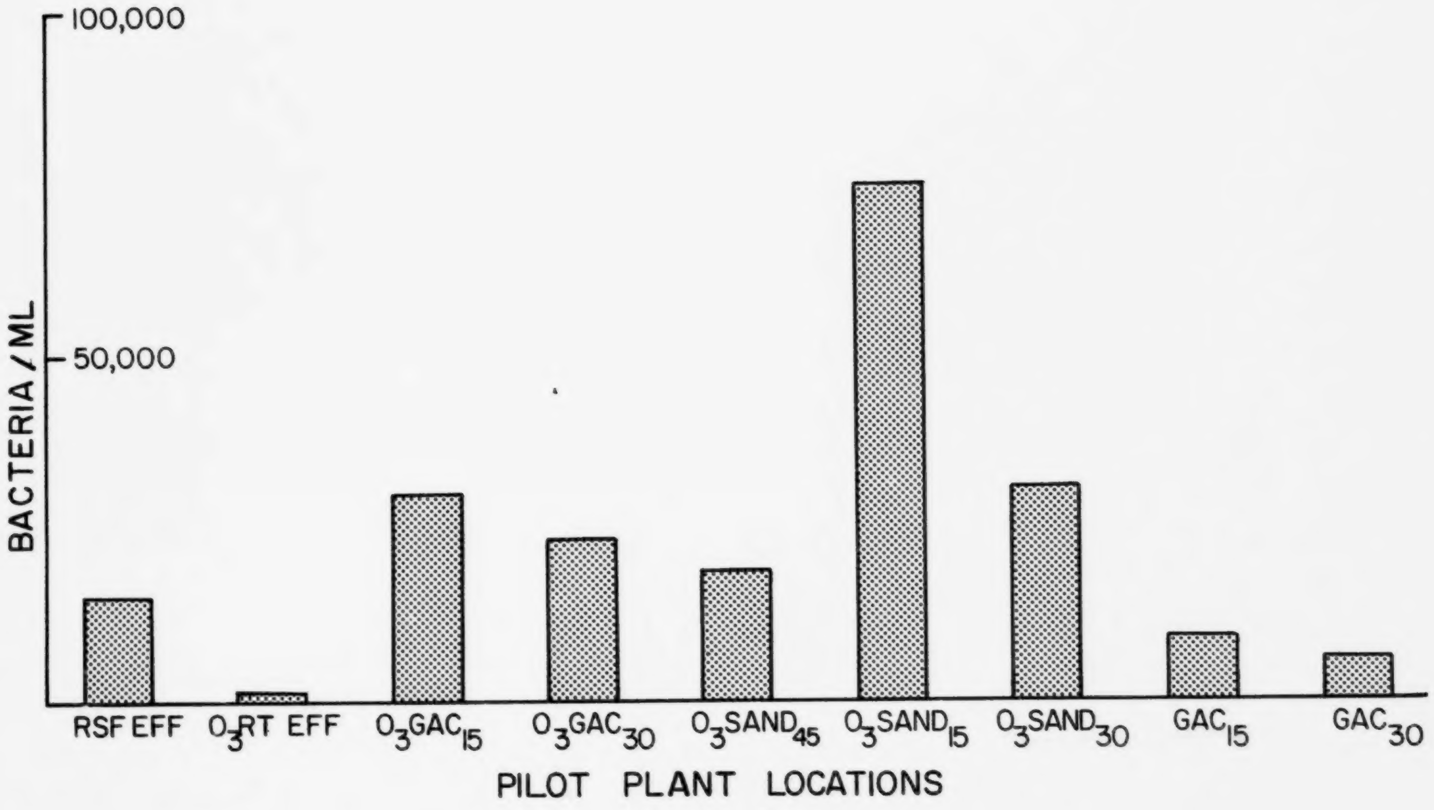

Figure 131. Average number of heterotrophic bacteria through the Pilot Plant.

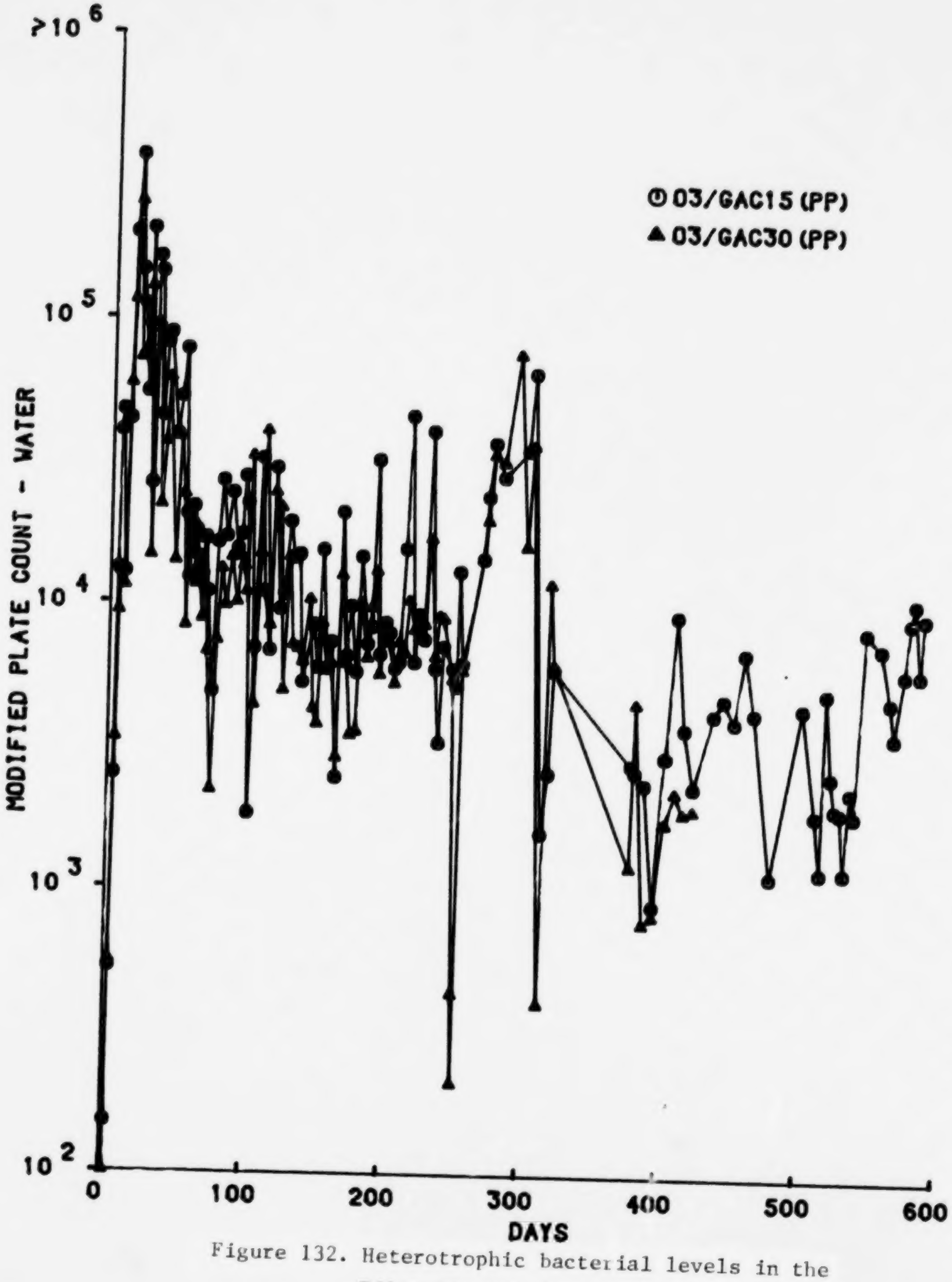

Figure 132. Heterotrophic bacterial levels in the Pilot Plant O_3/GAC system effluents.

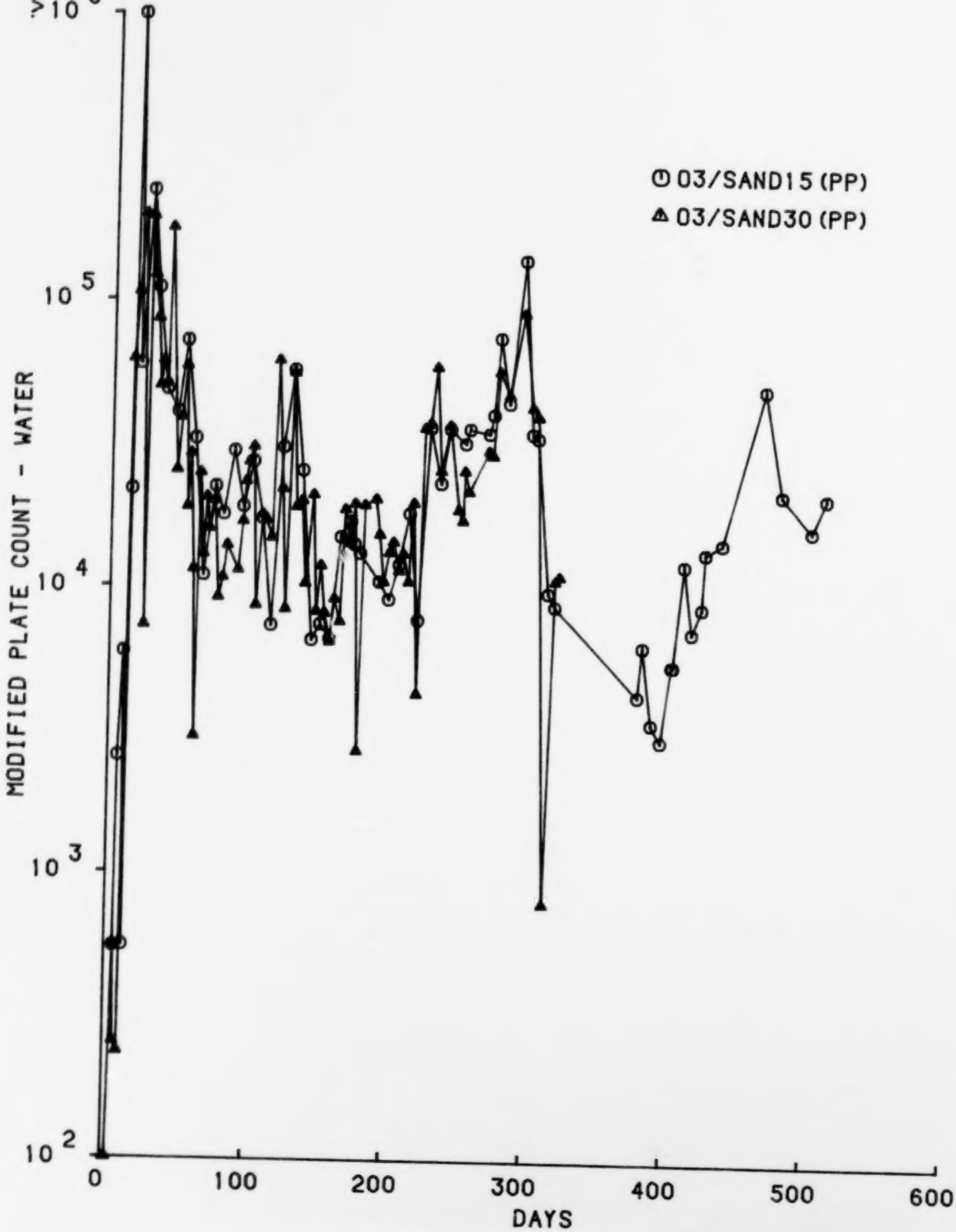

Figure 133. Heterotrophic bacterial levels in the Pilot Plant O_3/SAND system effluents.

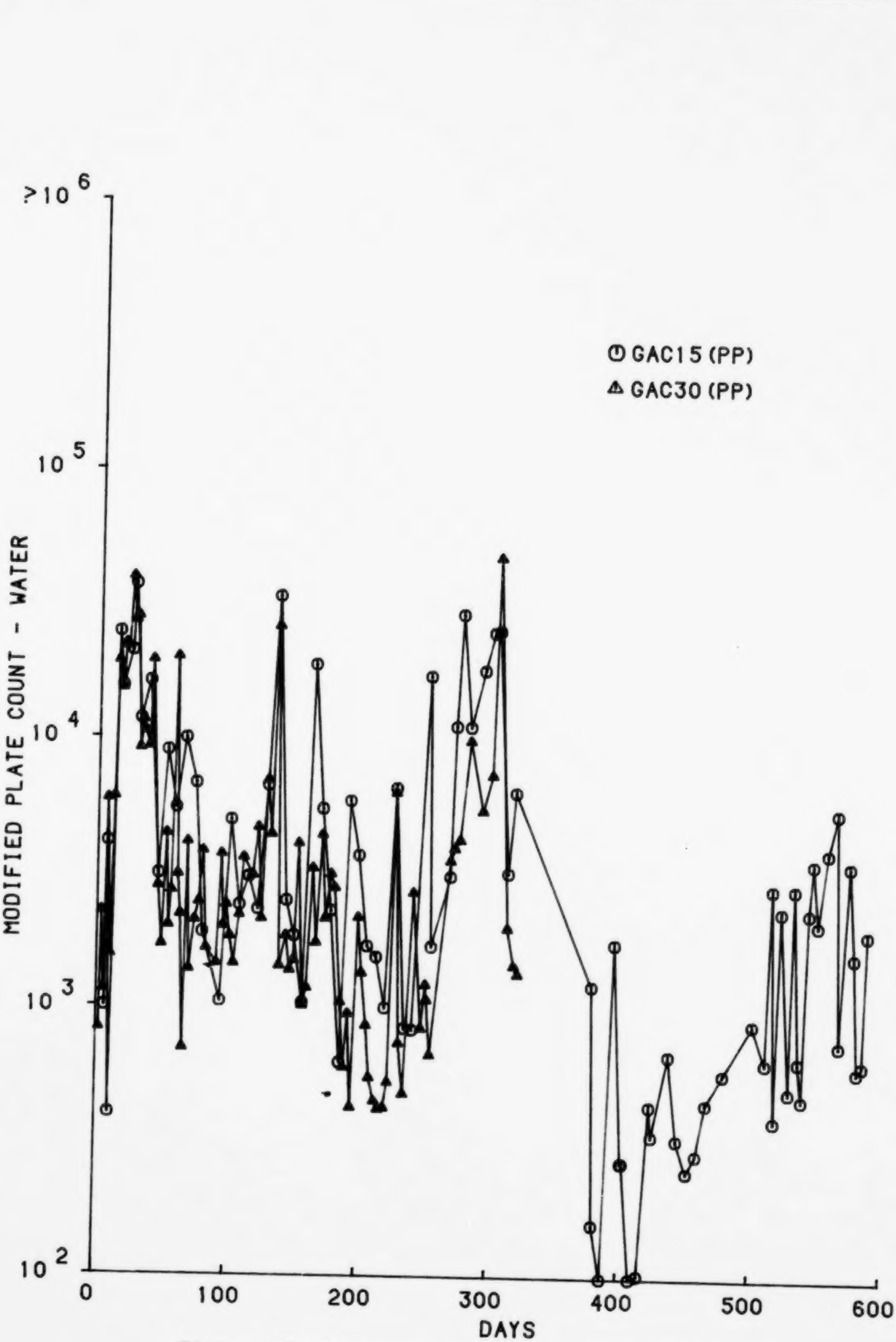

Figure 134. Heterotrophic bacterial levels in the Pilot Plant GAC system effluents.

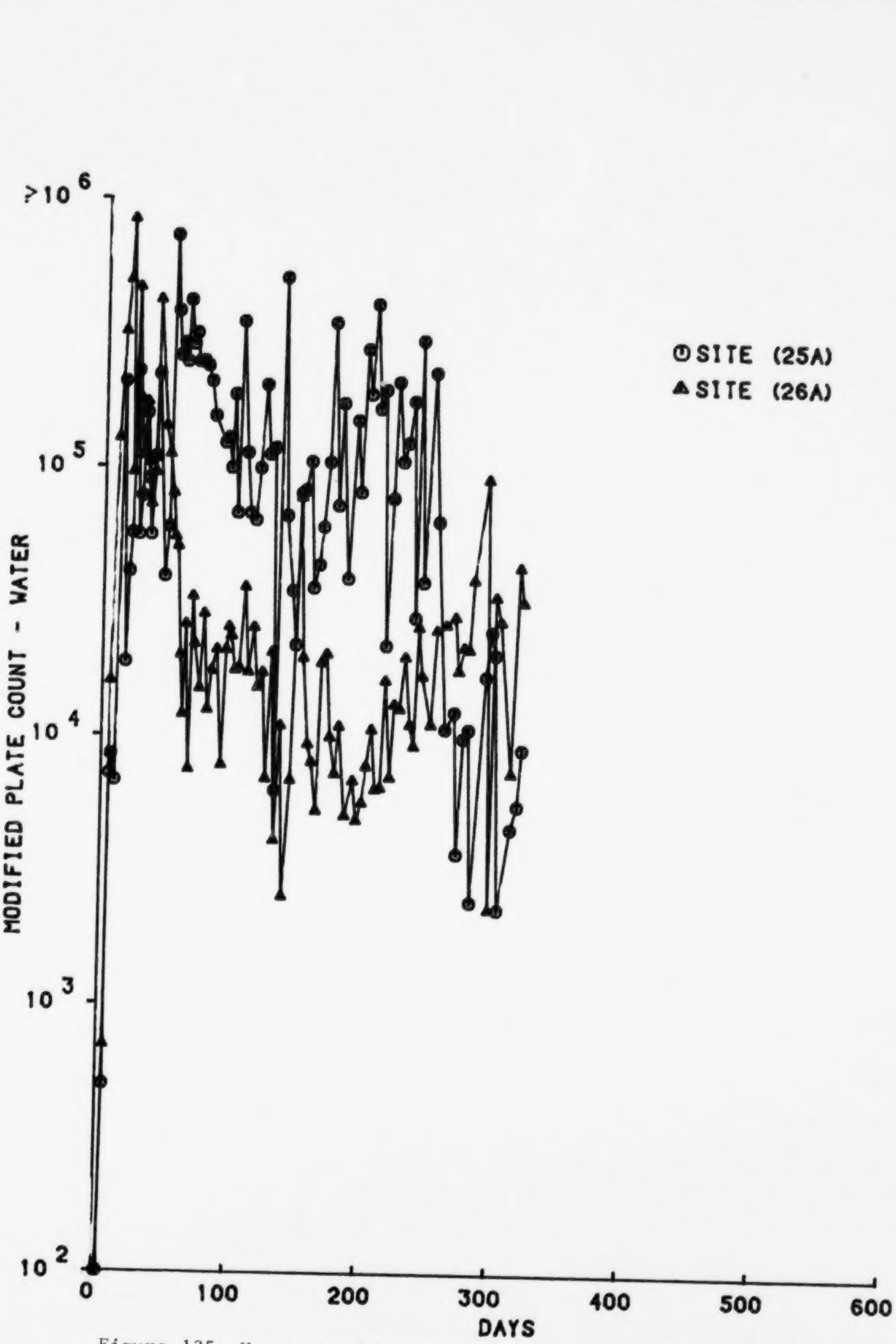

Figure 135. Heterotrophic bacterial levels in the Torresdale and Pilot Plant Multi-tap O_3/GAC system effluents.

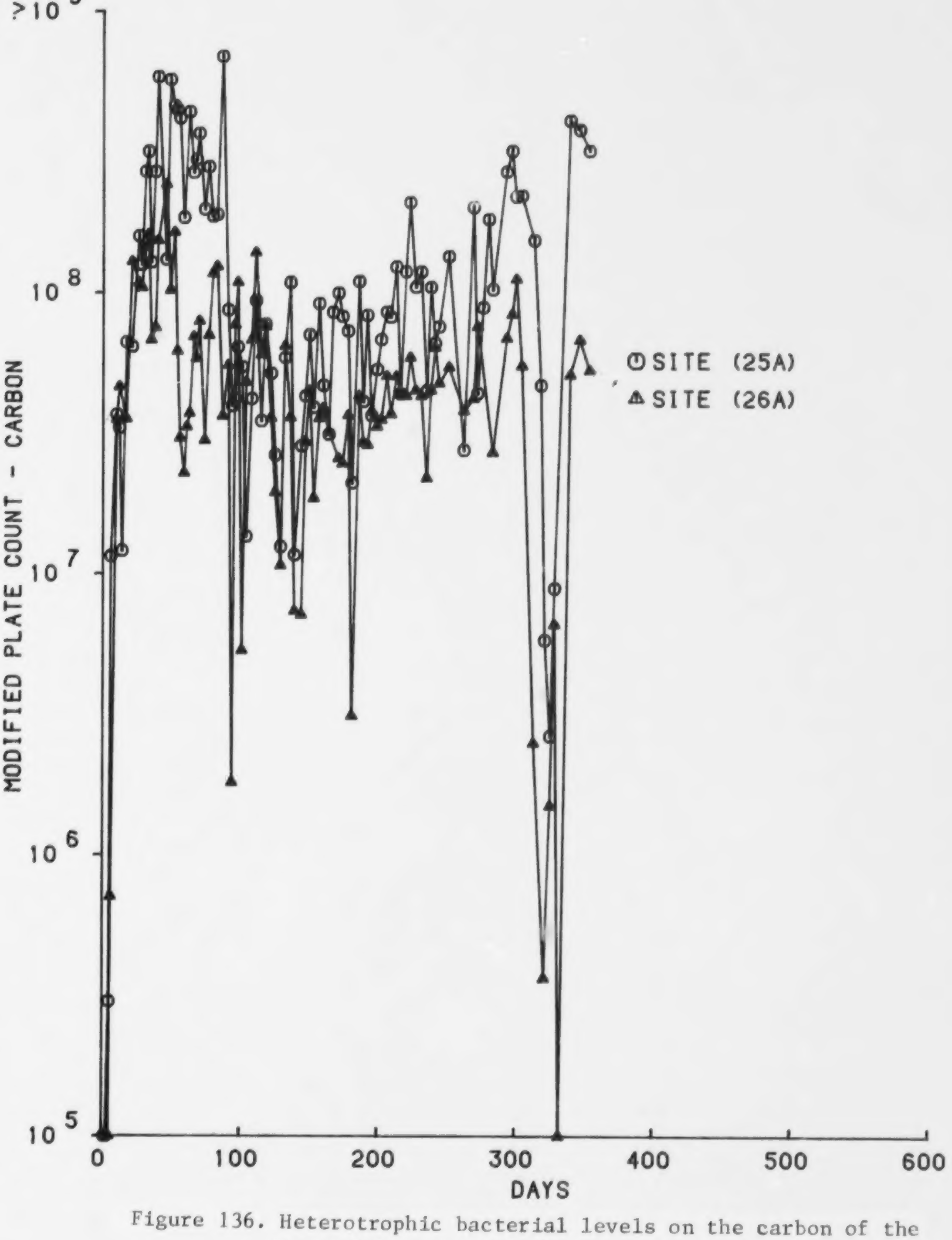

Figure 136. Heterotrophic bacterial levels on the carbon of the Torresdale and Pilot Plant Multi-tap O_3/GAC systems.

system. As was noted in the Torresdale system, bacterial species composition was similar in all the column effluents. Table 64 lists the bacteria isolated and identified in both the Torresdale and Pilot Plant systems. The most dominant organisms throughout the study were from the genera Flavobacterium and Pseudomonas. Bacillus sp. was again noted to be a predominant organism after the disinfection process, in this case, ozonation. Bacillus sp. was also found to be quite common in the non-ozonated carbon column effluents. Temperature again seemed to play a role in species composition as can be seen in Figure 137.

When the large carbon columns were dismantled carbon samples were removed from the middle of the beds. Figure 138 presents the bacterial counts in these columns. The bacteria identified from the carbon were the same species as those identified from the GAC column effluents.

Figure 139 illustrates the cumulative distribution functions of the microbial populations on the carbon columns (MT_{15}(PP), MT_{15}(TP)). Figure 140 illustrates the cumulative distribution functions of Torresdale and Pilot Plant $O_3/GAC_{15,30}$ effluent bacterial densities. Figures 141 and 142 illustrate the cumulative distribution functions of $GAC_{15,30}$ for the Torresdale and Pilot Plant; and O_3/GAC_{15} and $O_3/Sand_{15}$ effluent bacterial densities respectively. The results are consistent with final bacterial populations found in the 6 in. O_3/GAC(TP) and O_3/GAC(PP) columns at breakdown.

The counts of actinomycetes and fungi in GAC column effluents were also examined in this study. Actinomycetes levels at specific locations in the five treatment trains were presented in Table 65. As can be seen from this table the level of actinomycetes was significantly reduced through the various treatment trains. Elimination of fungal populations by the various treatment processes was also very effective as can be seen in Table 66.

Analysis for endotoxin levels in the column effluents and the Torresdale High Service water was done on a bi-weekly basis throughout this study. Table 67 presents the average concentration of endotoxin (mg/ml) in the effluents of the carbon and sand columns and also in the Torresdale High Service water. There was no significant difference between the average endotoxin levels in Torresdale potable waters and GAC and sand system effluents.

Chlorination Study--The effects of chlorine on bacterial levels in carbon column effluents was examined in this study. A preliminary study was conducted on untreated Delaware River water to determine whether or not agitation of the water was necessary for effective bacterial inactivation. A river water sample was adjusted to a pH of 8.5 and a temperature of 25°C and divided into four 300 ml portions. A chlorine residual of 2.0 ppm was established in two of these portions. Two non-chlorinated portions were used as controls. Agitation was provided by a Burrell Shaker. The results in Table 68 indicate that there was no apparent difference between agitated and non agitated chlorinated bacterial counts in the first 30 minutes. In 24 hours the inactivation process was slightly better in the agitated portion. All further studies were done on stationary samples.

TABLE 65. ACTINOMYCETE COUNTS FROM THE TORRESDALE AND PILOT PLANT TREATMENT TRAINS FROM 5/80 TO 2/81

Location	Mean (x) (counts/100 ml)	S.D.	Max.	Min.
RIVER	18200	12300	50000	0
GAC_{30} (TP)	175	310	1300	0
O_3/GAC_{30} (PP)	33	90	400	0
$O_3/SAND_{15}$ (PP)	20	50	200	0
$O_3/SAND_{30}$ (PP)	30	70	300	0
GAC_{30} (PP)	46	90	300	0
$MT_{7.5}$ (TP)	33	120	600	0
MT_{15} (PP)	100	450	2200	0

MT - Multitap Columns

TABLE 66. FUNGUS COUNTS IN THE TORRESDALE AND PILOT PLANT TREATMENT TRAINS FROM 5/8 TO 2/81

Location	Mean (x) (counts/ml)	S.D.	Max.	Min.
RIVER	17700	14900	50000	7
GAC_{30} (TP)	110	70	200	0
O_3/GAC_{30} (PP)	110	60	300	0
$O_3/SAND_{15}$ (PP)	70	100	400	0
$O_3/SAND_{30}$ (PP)	60	140	600	0
GAC_{30} (PP)	100	80	300	0
$MT_{7.5}$ (TP)	90	140	600	0
MT_{15} (PP)	70	60	200	0

MT - Multitap Columns

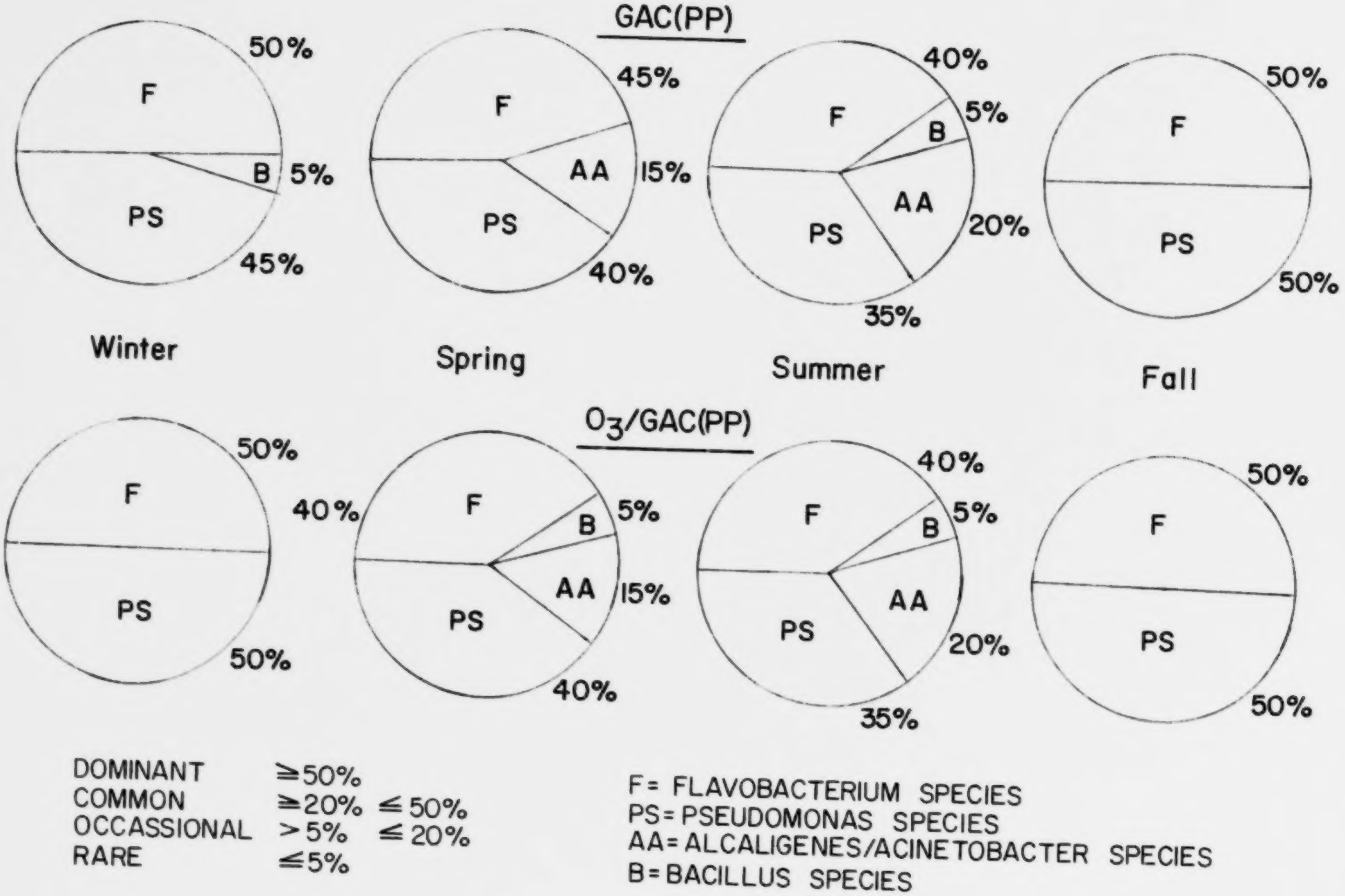

Figure 137. The composition of heterotrophic bacteria isolated in the Pilot Plant adsorption system effluents (4/80 to 3/81).

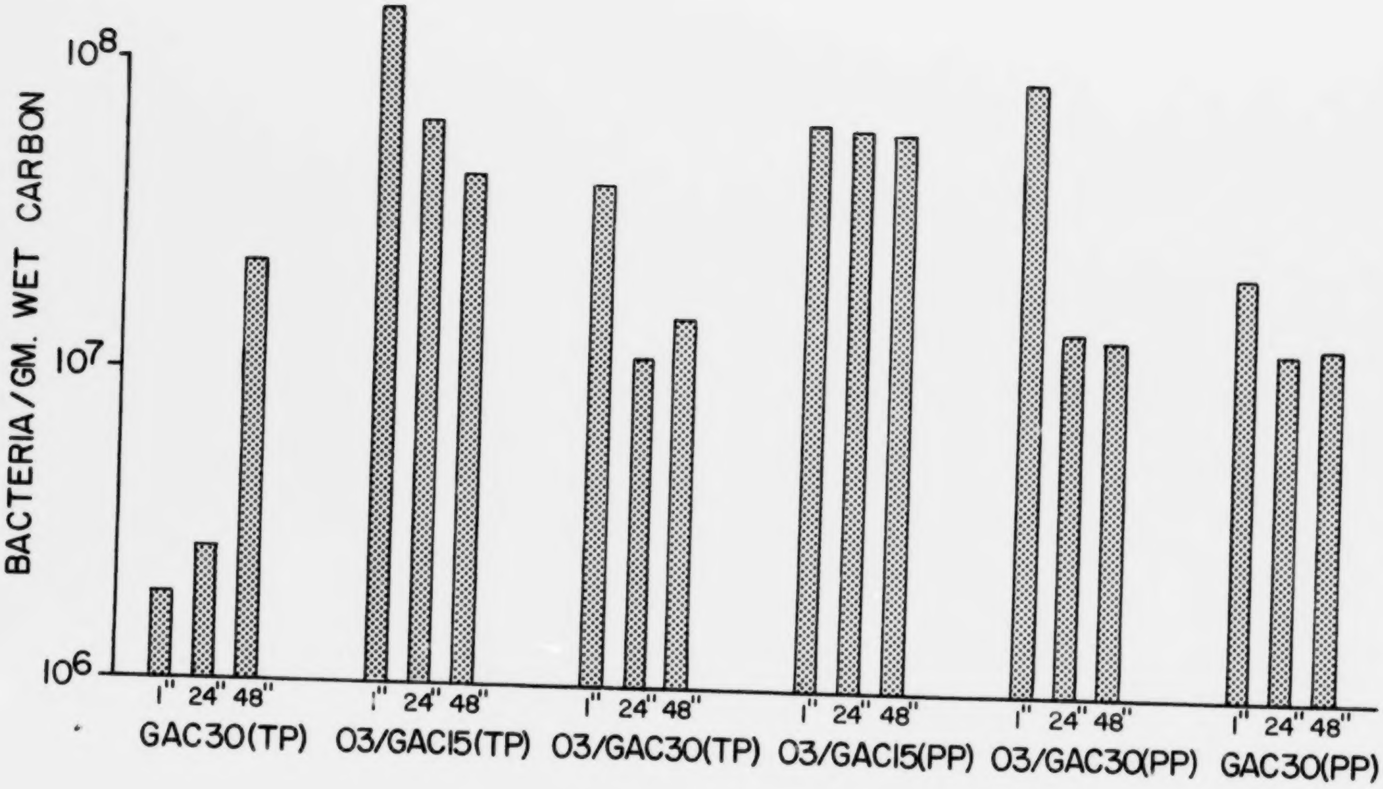

Figure 138. Heterotrophic bacterial levels on the carbon at various depths in the column at the end of the study.

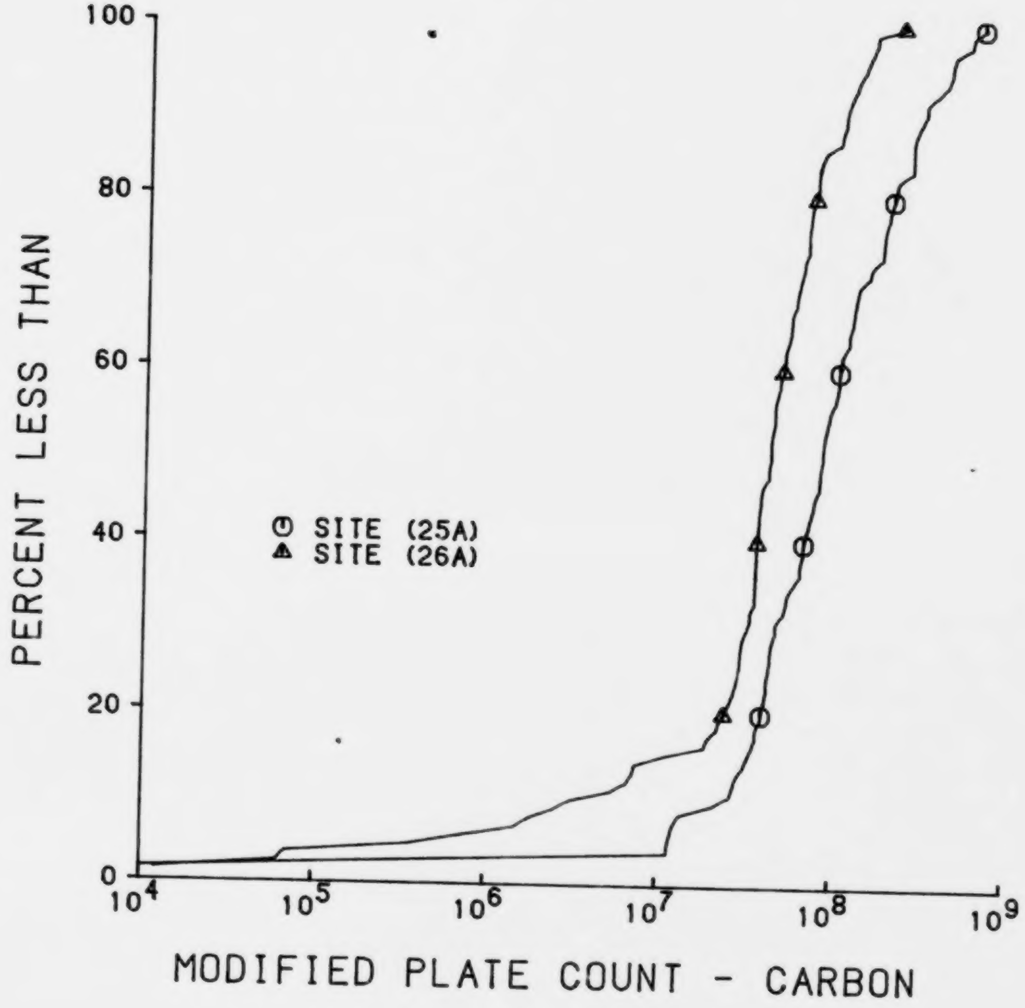

Figure 139. Bacteria on the carbon in the Multi-tap GAC Systems.

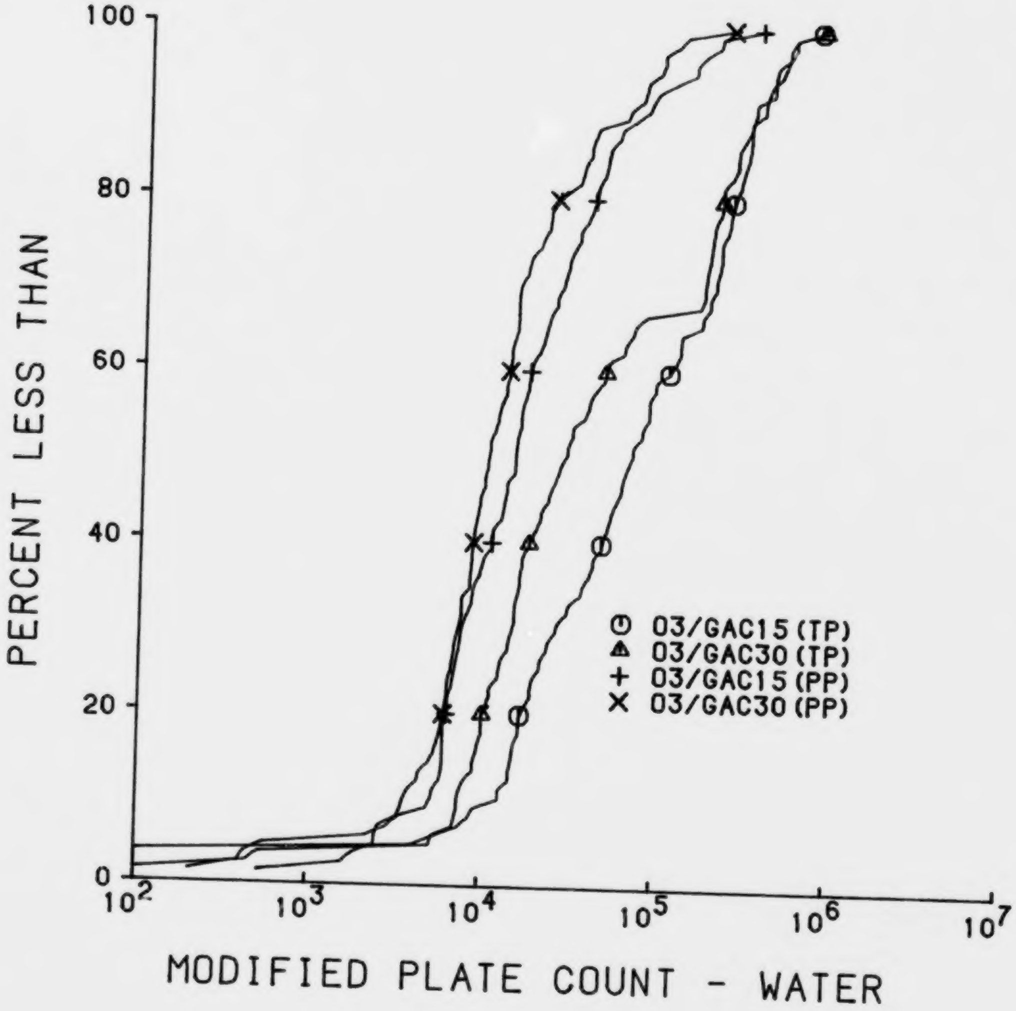

Figure 140. Bacteria in the effluents of O_3/GAC systems.

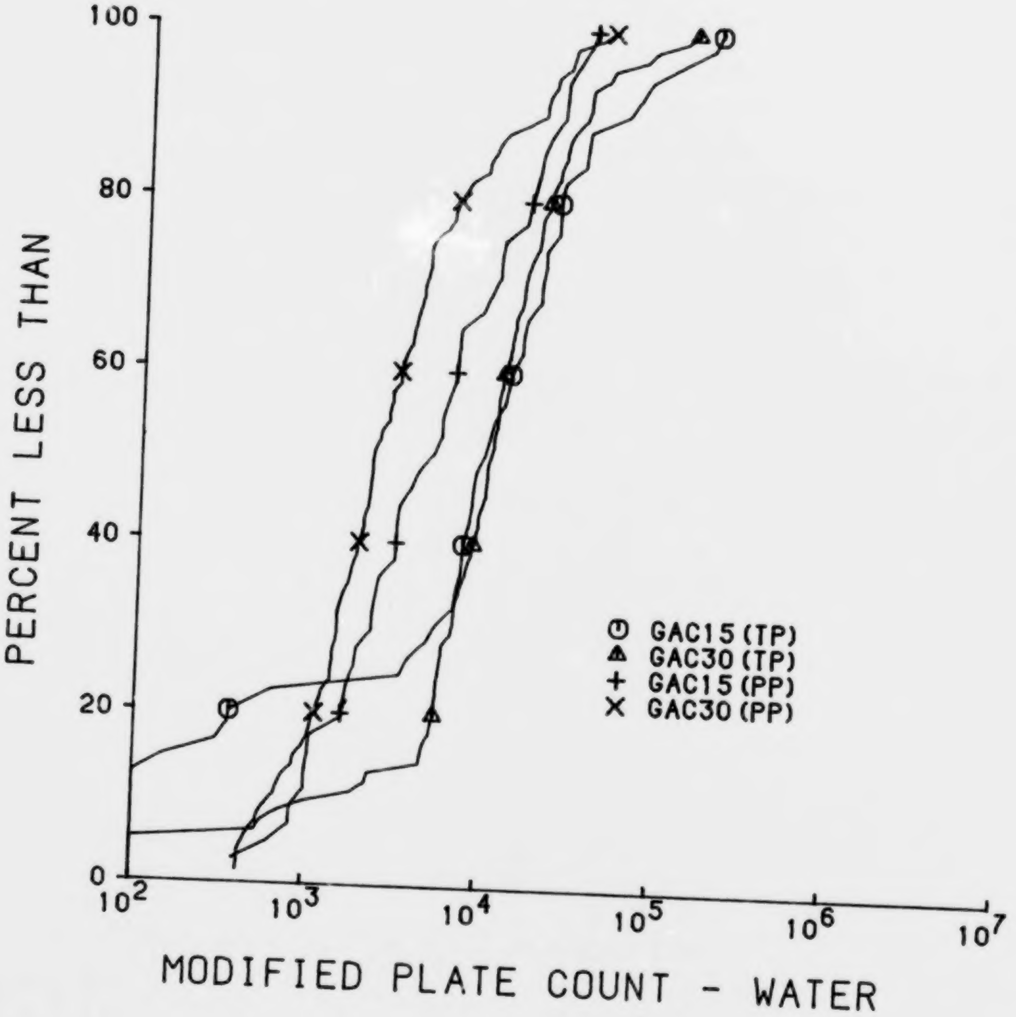

Figure 141. Bacteria in the effluents of GAC systems.

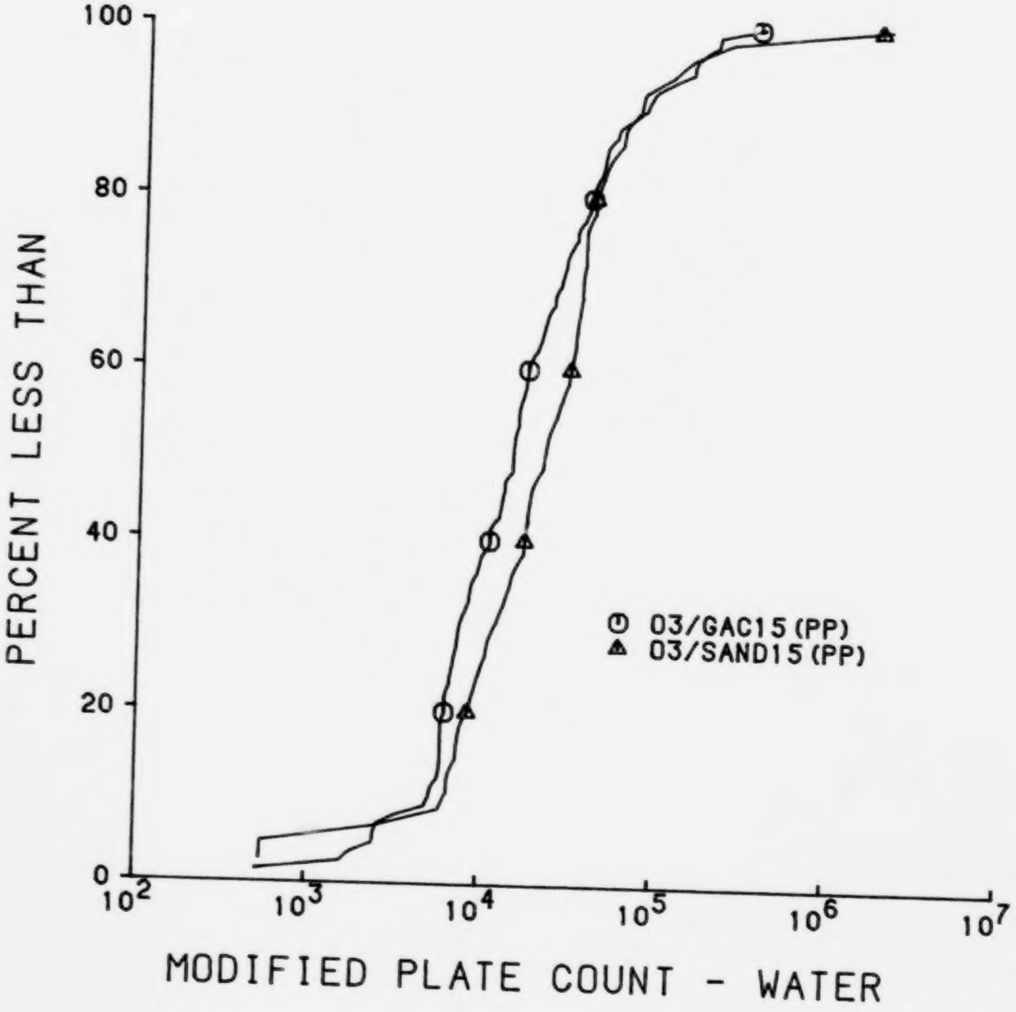

Figure 142. Bacteria in the effluents of O_3/GAC and O_3/SAND systems (15 min. EBCT).

TABLE 67. ENDOTOXIN LEVELS (ng/l) IN THE TORRESDALE AND PILOT PLANT TREATMENT TRAINS AND TORRESDALE HIGH SERVICE

Location	Mean (x) Endotoxin (nanograms/nl)	S.D.	Max.	Min.
GAC_{15} (TP)	35.8	32.86	82.92	3.92
O_3/GAC_{15} (PP)	36.6	26.40	90.62	9.82
$O_3/SAND_{15}$ (PP)	36.3	22.74	77.54	1.99
GAC_{30} (PP)	37.1	32.67	10.38	2.15
$MT_{7.5}$ (TP)	18.5	11.21	42.95	20.08
MT_{15} (PP)	37.8	30.58	90.77	10.00
Torresdale High Service Water	34.1	27.48	86.77	25.35

MT- Multitap Columns

A second series of chlorine tests was conducted on Pilot Plant column effluents. Each sample was adjusted to a pH of 8.5 at 25°C and divided into two 300 ml portions, one of which was chlorinated and the other was used as a control. Aliquots of both portions were taken at 2, 30, 60, 120 minutes and 24 hours for AFAH bacterial counts and chlorine measurements. Results of this study can be found in Table 69. These results indicate that inactivation was immediate and no regrowth was detected in 24 hours time.

TABLE 68. BACTERIAL INACTIVATION IN AN AGITATED AND NONAGITATED RIVER SAMPLE DOSED WITH CHLORINE

Sample	Free Chlorine Residual (mg/L)		Total Bacteria Counts (per/ml)			
			Non-Chlorinated		Chlorinated	
	Stationary	Agitated	Stationary	Agitated	Stationary	Agitated
2 Min.	2.0	2.0	114000	93000	387	285
30 Min.	0.7	0.7	120000	105000	333	392
24 Hour	0.1	0.1	147000	119000	333	209

Scanning Electron Microscopy Study--Carbon particles from a carbon column with a 60 minute empty bed contact time (EBCT) were examined under the electron microscope to determine the number and location of bacteria on a carbon particle. The carbon column was on-line at the Torresdale Plant utilizing Torresdale pretreated water for 6 weeks. Figure 143 is a representative electron micrograph of bacterial populations on carbon particles. As can be seen from this micrograph, bacterial populations were found clumped in the crevices and macropores of the carbon particles while the shear surfaces of the particle were found to be devoid of microbial life. The initial purpose of this study was to determine the total number of bacteria on a carbon particle. However, the nonuniform clumped population patterns found on the carbon made it impossible to accurately determine the total bacterial population of a carbon particle. Consequently visual examination of over a hundred different micrographs was done and the following conclusions were drawn from these observations. Bacterial populations were not found to form a "biofilm" around the entire carbon particle as was previously hypothesized by Benedek (11) but instead were found in distinct population centers which were primarily located in particle crevices and macropores. Particles with heavy surface residues of iron and calcium were not as heavily populated as residue free particles. Mixed populations of rods, cocci and actinomycetes filaments were found in the clumped population centers and many of these bacteria developed fimbriae in order to attach themselves to the carbon surface. Moreover, these bacteria were found to be in various stages of development, including cell division which indicates that bacterial multiplication occured in the carbon beds.

Backwash Study -- At the beginning of this project, concern was expressed over the column backwash process and its effect on the bacterial levels in the column effluents. In May of 1980 a backwash study was conducted to determine the levels of Coliform and AFAH Bacteria in the pre and post backwashed column effluents. The results of this study can be found in Tables 70 and 71. Significant increases in both the coliform and AFAH bacterial levels were noted. However, these levels decreased with time. The effect of backwashing on the bacterial populations on the carbon could not be determined in this study.

MINI-COLUMN STUDIES

The results of the five experiments conducted on the mini columns for determining the relative contributions of adsorptive and biological TOC removal are presented in the following pages. A discussion of the implications of these studies and the parallel studies at the pilot plant on each other will be presented in the discussion section.

Oxygen Uptake on GAC

Experiments were completed to determine whether dissolved oxygen could be used as an indirect measure of bioactivity in a GAC adsorption system. To do this, an attempt was made to separate chemical and biological reactions with dissolved oxygen on GAC. An initial experiment used a series of Millipore filter cartridges (0.22 μm Durapore Cartridge #CVGL010P1) to try to

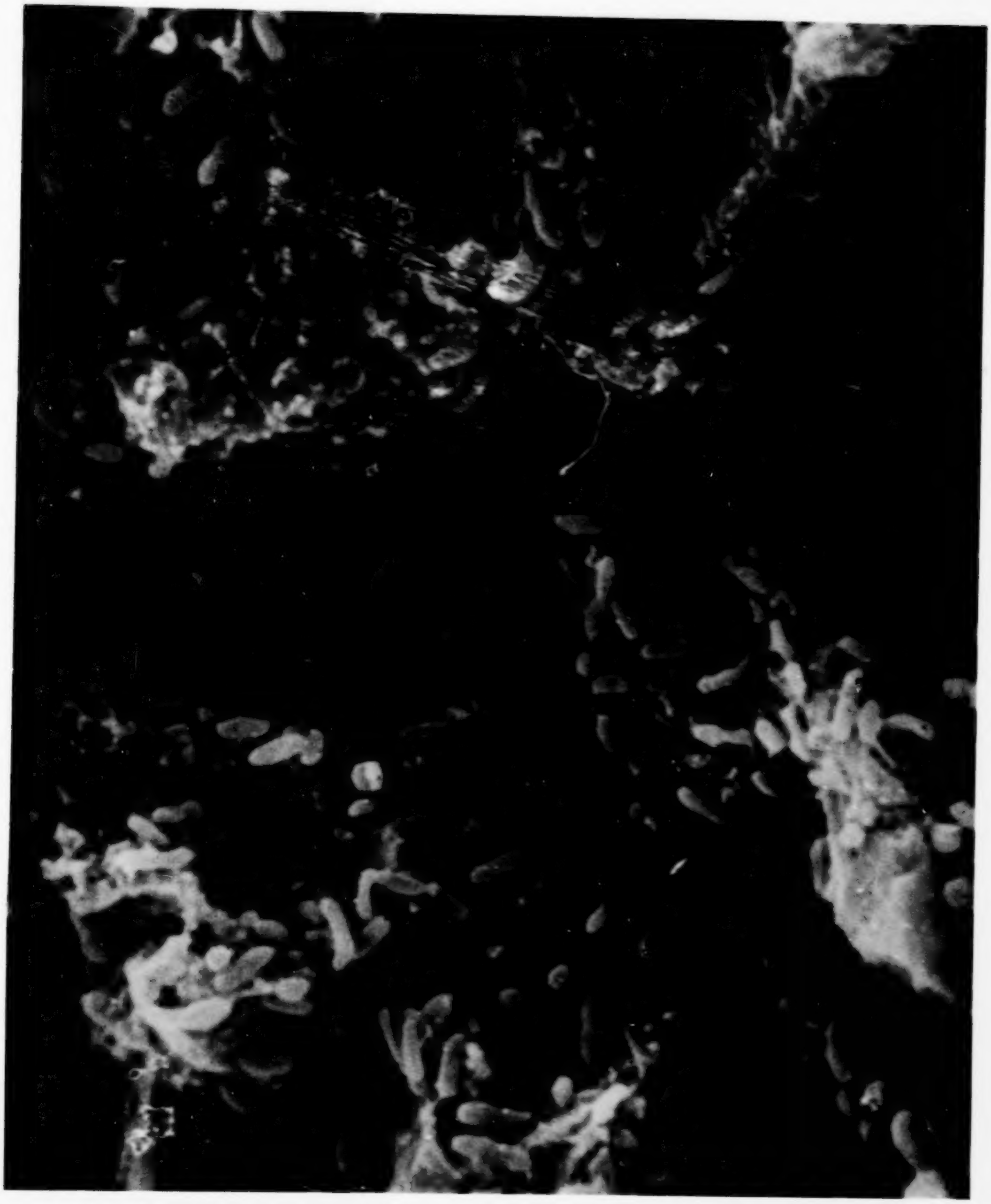

Figure 143. Electron micrograph of carbon particle.

TABLE 69. BACTERIAL INACTIVATION IN PILOT PLANT EFFLUENTS USING CHLORINE

Time	Free Chlorine Residual	Sample Location	Non-Chlorinated Bacteria/ml	S.D.	Chlorinated Bacteria/ml	S.D.
2 Min	2.50	O_3/GAC_{15} (PP)	6790	103	0.2	0.4
30 Min	2.40		6810	78	0.3	0.4
60 Min	2.35		6485	45	0.0	0.0
120 Min	2.30		6865	66	0.2	0.4
24 Hours	2.00		7380	51	0.1	0.3
2 Min	2.00	$O_3/SAND_{15}$ (PP)	11150	210	0.4	0.4
30 Min	1.90		8600	200	0.1	0.3
60 Min	1.80		22000	278	0.1	0.3
120 Min	1.70		20000	114	0.4	0.4
24 Hours	0.90		152000	134	0.0	0.0
2 Min	2.00	O_3/GAC_{30} (PP)	59800	225	0.8	1.2
30 Min	1.90		55000	230	0.1	0.3
60 Min	1.85		57200	163	0.0	0.0
120 Min	1.80		50400	187	0.1	0.3
24 Hours	1.30		380000	246	0.5	0.9
2 Min	2.0	O_3/GAC_{30} (PP)	1200	14	6.8	1.7
30 Min	1.8		2400	34	3.6	1.5
120 Min	1.6		1600	15	3.0	1.2
24 Hours	1.4		27100	188	1.0	0.5
5 Days	1.1		25200	85	1.0	0.4
2 Min	2.1	O_3/GAC_{30} (PP)	6150	58	0.4	0.8
30 Min	1.7		4800	56	1.0	0.6
120 Min	1.5		8100	40	0.2	0.4
24 days	0.9		63800	148	0.4	0.5
5 days	0.2		27300	134	0.0	0.0

TABLE 70. AFAH BACTERIAL LEVELS IN COLUMN EFFLUENTS BEFORE & AFTER THE BACKWASH PROCESS

	AFAH Bacteria (counts/ml)				
Location	Before Backwash	Backwash Water	Col. Eff. 1.5 min.	Col. Eff. 3 min.	Col. Eff. 6 min.
GAC_{15}(TP)	80,000	1,600	154,000	716,000	400,000
O_3/GAC_{15}(TP)	480,000	250	135,000	10,000,000	5,000,000
O_3/GAC_{15}(PP)	890,000	30,000	3,700,000	3,000,000	1,000,000
GAC_{15}(PP)	25,000	30,000	1,300,000	250,000	220,000

TABLE 71. TOTAL COLIFORM LEVELS IN COLUMN BACKWASH WATERS AND COLUMN EFFLUENTS AFTER BACKWASH

	Total Coliforms/100ml			
Column Location	GAC_{15}(TP)	O_3/GAC_{15}(TP)	O_3/GAC_{15}(PP)	GAC_{15}(PP)
Backwash Water	9	3	12	18
Column Effluent (1 Min)	30	0	30	760
Column Effluent (3 Min)	10	0	20	60
Column Effluent (15 Min)	0	0	0	0

maintain sterile conditions in a laboratory GAC system for a period of 17 days. The purpose of the experiment was to determine whether dissolved oxygen removal could be lowered to a negligible amount by removing bacteria from the system.

Dissolved oxygen removal was monitored for seventeen days, using the apparatus shown previously in Figure 14. Distilled water was recycled by a positive displacement pump and the oxygen level was maintained near saturation by diffusing compressed air into the reservoir. For this experimental study, the TOC was monitored by a Beckman 915A TOC Analyzer. The TOC response in the effluent of the GAC contactors was always less than the response from the 0 mg/l standard (fresh distilled water) used for the Beckman analyzer, thus no data other than "below limit of detection" is available for this study.

The presence or absence of bacteria was observed by plate count without dilution. Therefore, bacterial density was only measured in terms of "0" or ">0" i.e. sterile or nonsterile. The Millipore filter cartridges proved ineffective in removing bacteria, as the first sample and all subsequent samples from the filtered contactor effluent proved positive for colony forming units (cfu). No density data are available, but the presence of bacteria was observed in the effluents of all contactors. Apparently the organisms were growing through the filter.

Although a sterile system was not attained, biodegradable material is assumed to be in very low concentration in the reservoir because it was recycled distilled water without any nutrient input. Furthermore, the TOC response was always less than in freshly distilled water. Figure 144 shows the dissolved oxygen results for the four contactors. No differentiation is made between contactors here because none were sterile and all received a common influent. Note that all contactors had a reproducible oxygen breakthrough profile and that a steady state oxygen uptake appears to occur after 200 hours. This data is in general agreement with (123) who showed that dissolved oxygen removal by GAC rapidly reached a plateau and that removal lasted at least 1700 hours (i.e., oxygen removal continued until the end of the experimental time utilized).

The failure to achieve a zero level of oxygen removal indicates that dissolved oxygen may not be a viable technique for indirect measurement of bioactivity. Prober et. al. found that surface oxides increased after GAC had been exposed to aqueous oxygen suggests that a chemical reaction was occurring between oxygen and GAC (123). Thus, some estimate of the chemical oxygen demand would be required prior to estimating bioactivity by dissolved oxygen consumption. The use of dissolved oxygen consumption in this manner will be addressed in further experiments and the discussion section.

Adsorption Reproducibility

The purpose of this experiment was to determine if column studies were reproducible under the experimental setup utilized herein. This gives a baseline of error which must be exceeded prior to drawing conclusions about the significance of data from parallel contactors. This experiment also

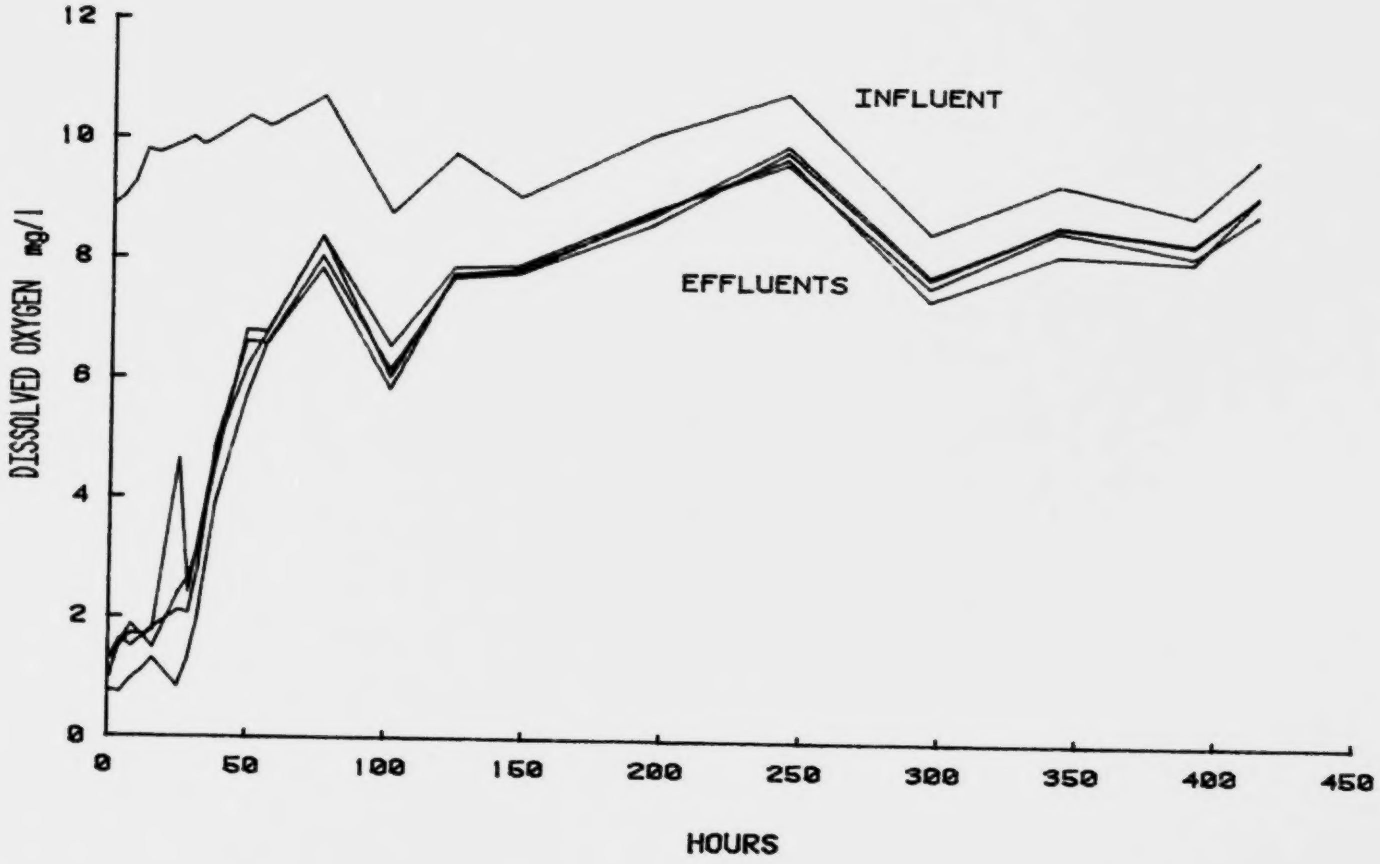

Figure 144. DO removal across a GAC contactor using recycled distilled water.

tested the hypothesis that temperature would have negligible effects on the adsorption of TOC (129) across the contactors used in this study. Demonstration of negligible effects of temperature on adsorption in the GAC contactors used in this study becomes important later when comparing biological and adsorptive TOC removals.

This experiment involved eight identical contactors receiving a common influent during the initial phase and thus allowed a quality control comparison for identical contactors as well as an examination of the contribution of bacteria to organic removal and effect of temperature on the selected parameters during the first eleven weeks of GAC contactor operation.

Figures 145 and 146 show the effect of the carbon adsorption unit process on the parameters pH and alkalinity. Values plotted are for the influent, effluent of contactors 7 and 8, and the contactor next in line to be broken down (see Figure 16). Two modes of operation are shown on the figures; ambient (Mode A) and ambient-chilled (Mode B). The parameters in these figures show no consistent trend due to carbon treatment or temperature differential.

Figures 147 and 148 show the effect of the carbon adsorption unit process on TOC and absorbence at 254 nm (A254). Values are plotted for the influent, effluents of contactors 7 and 8, and the contactor next in line to be broken down. These parameters do show a strong effect of the adsorption process but are not affected by the temperature differential for the first 250 days on line. These parameters show good reproducibility between contactors. There is some scatter in the TOC values in the initial samples, but this is not unusual in that the values are quite low and near the instruments detection level of 100 ppb (See Appendix A).

Cross comparison of the influent values for TOC and A254 shows higher variability in the A254 than in TOC. It is observed that even peak maxima are not consistent. Several investigators (e.g. (40)) have used A254 as a rapid measure of TOC after showing a correlation between A254 and TOC for raw river water. Figure 149 shows the absence of an overall relationship between TOC and A254 for the sand filtered, ozonated water used in this study. The influent water for this study came directly from an ozone contactor. Ozone does not oxidize TOC to CO_2 at the concentrations used in this study (ozone applied dose = 1.2 mg/l, ozone residual in effluent of ozonator = 0.3 mg/l and ozone utilized of 1.2 mg/l), but it appears effective in reducing aromaticity. The lack of correlation between TOC and A254 shows that A254 cannot be used as a rapid measure of TOC for water directly from the ozone contactor. The effluents showed the same trend of slow rise in both A254 and TOC, however, the values for the effluents were not analyzed (for correlation) because of the lack of a correlation for the influents. The lack of correlation was confirmed in the Pilot Plant run.

The purpose of this study was to separate the effects of adsorption and biodegradation on long term TOC removal in GAC contactors. A254 was meant to be a measure of TOC which could be a time saver. The absence of a correlation for the influents led to dropping A254 from the analysis in later

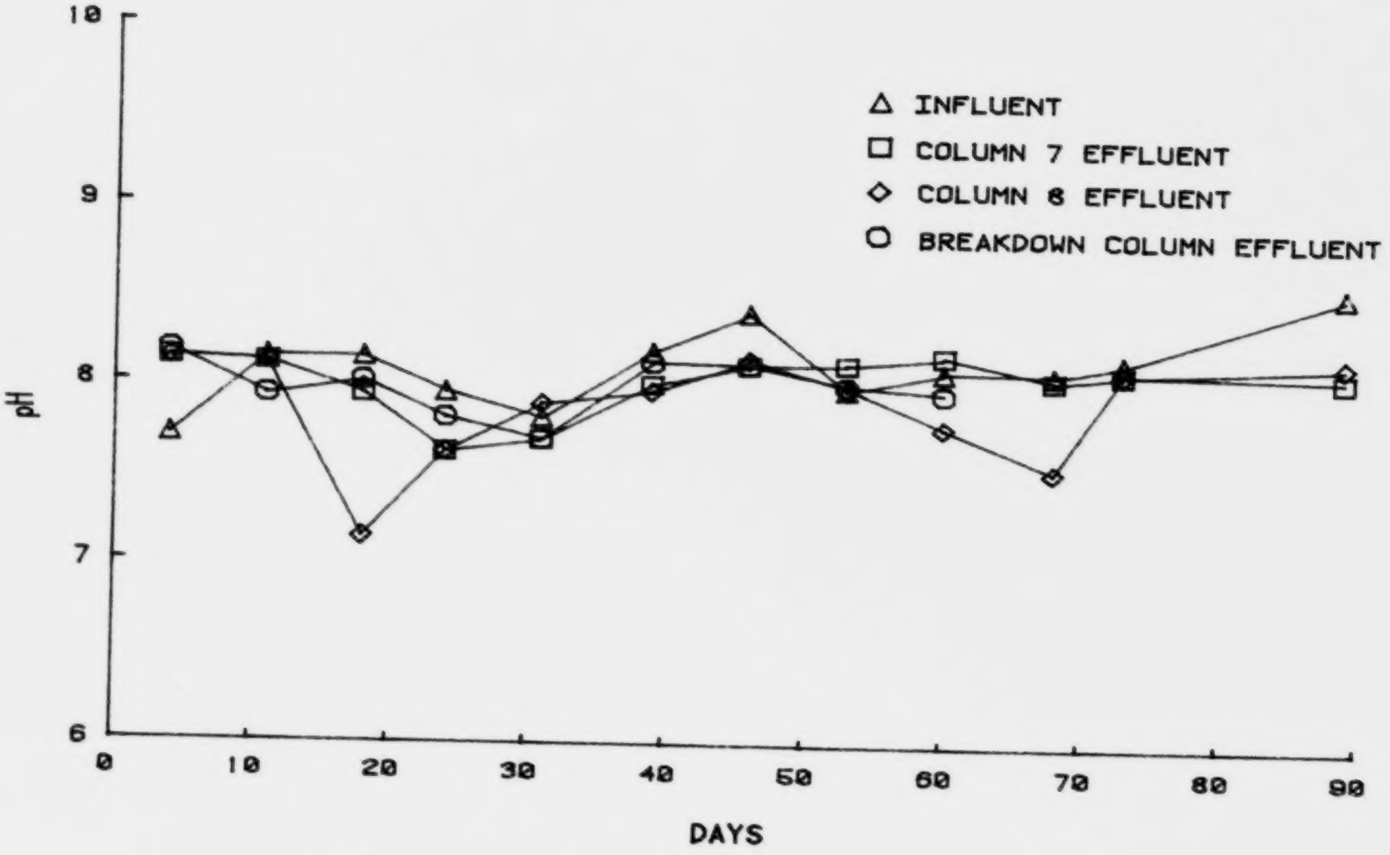

Figure 145. pH profile across GAC contactor (Mini-Column Study).

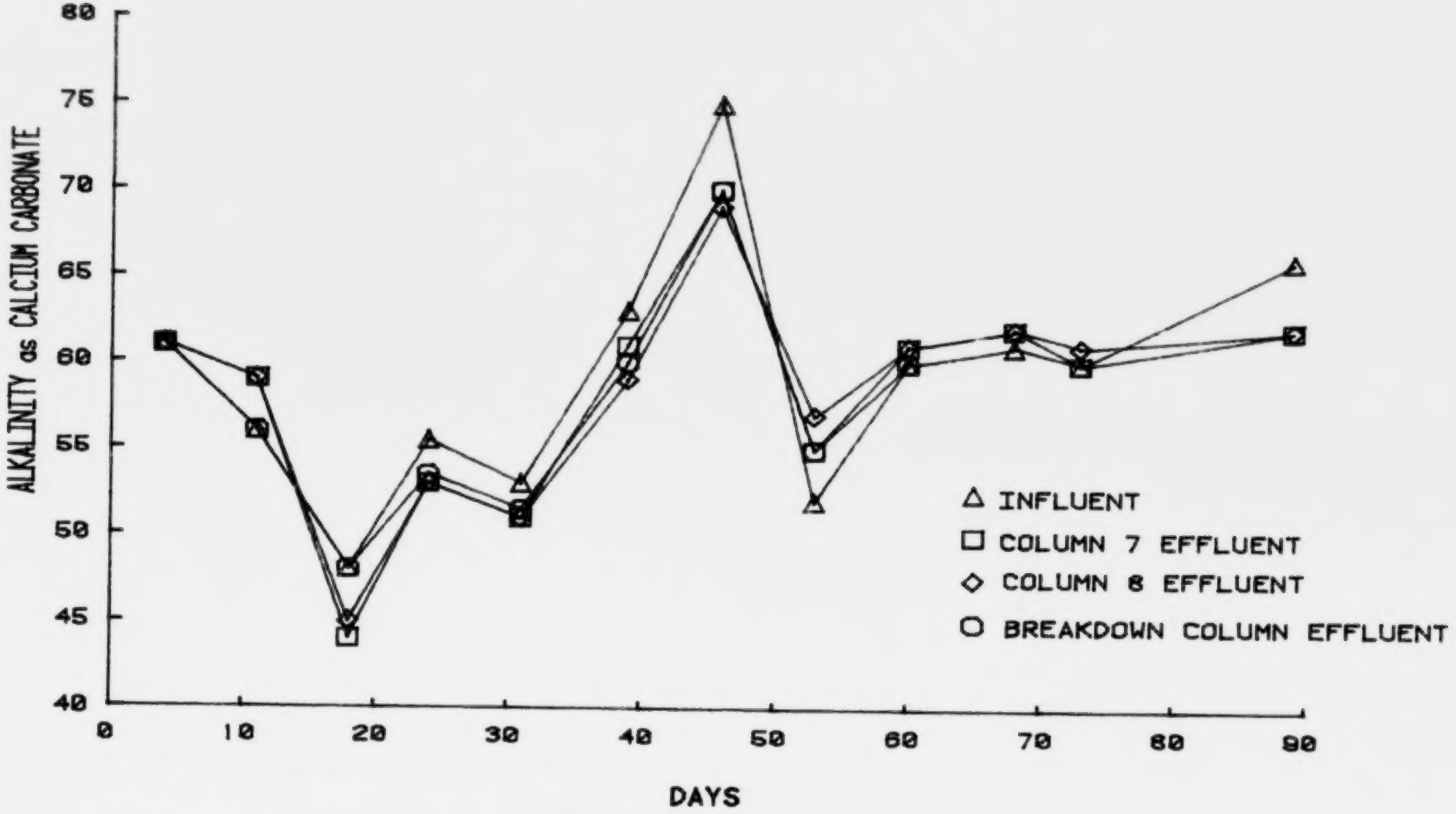

Figure 146. Alkalinity profile across GAC contactor (Mini-Column Study).

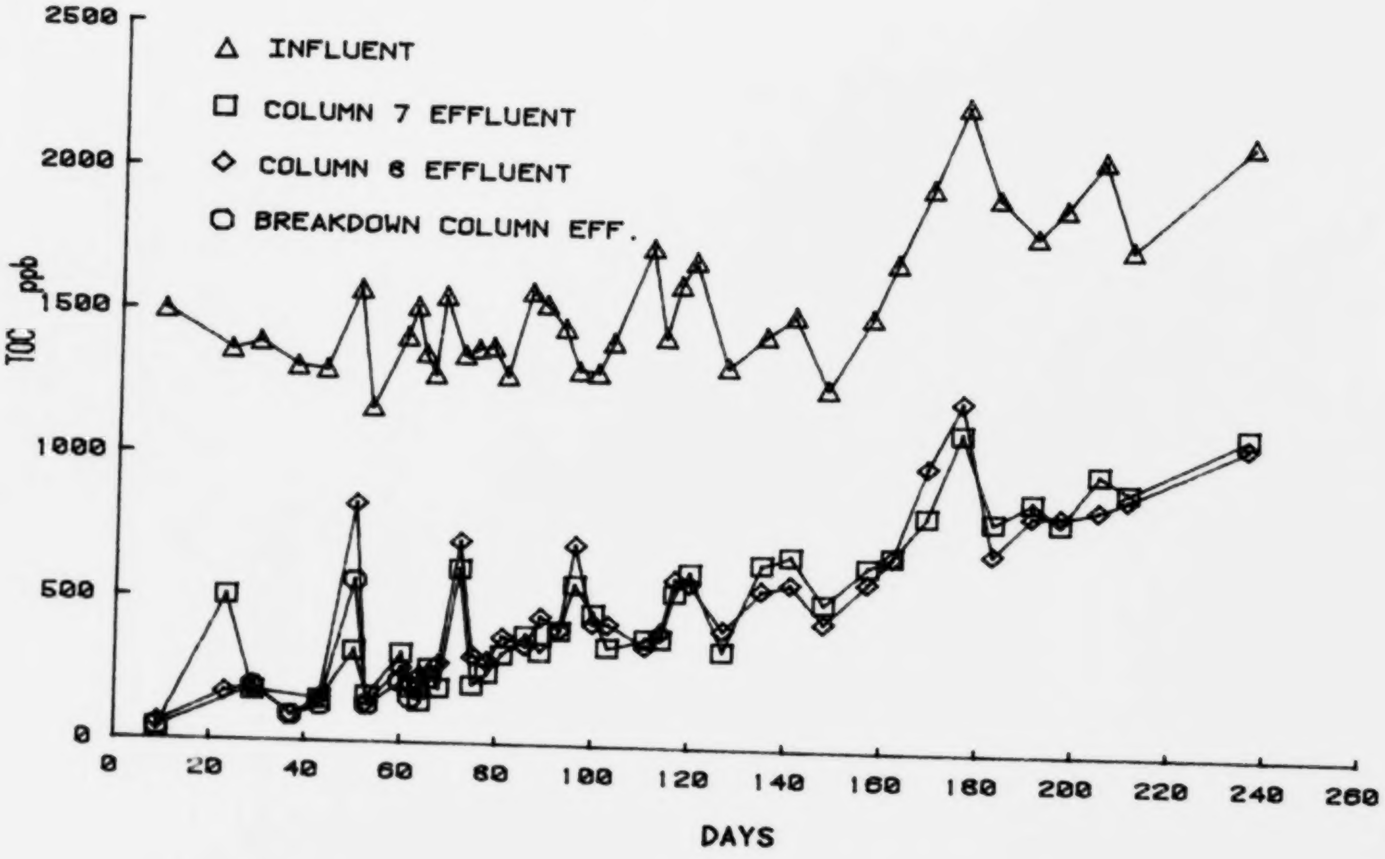

Figure 147. TOC profile across GAC contactor (Reproducibility Study).

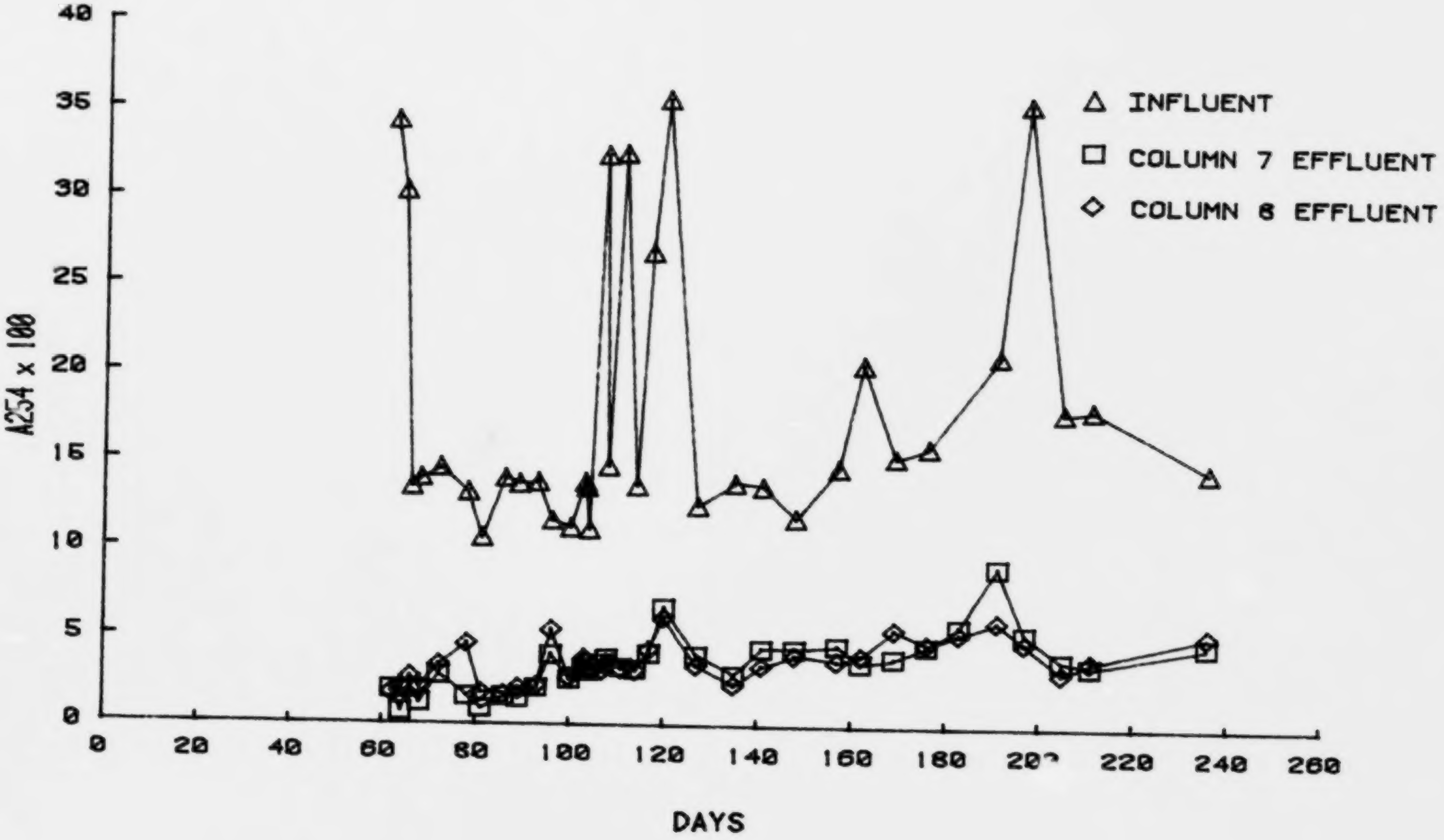

Figure 148. A254 profile across GAC contactor (Reproducibility Study).

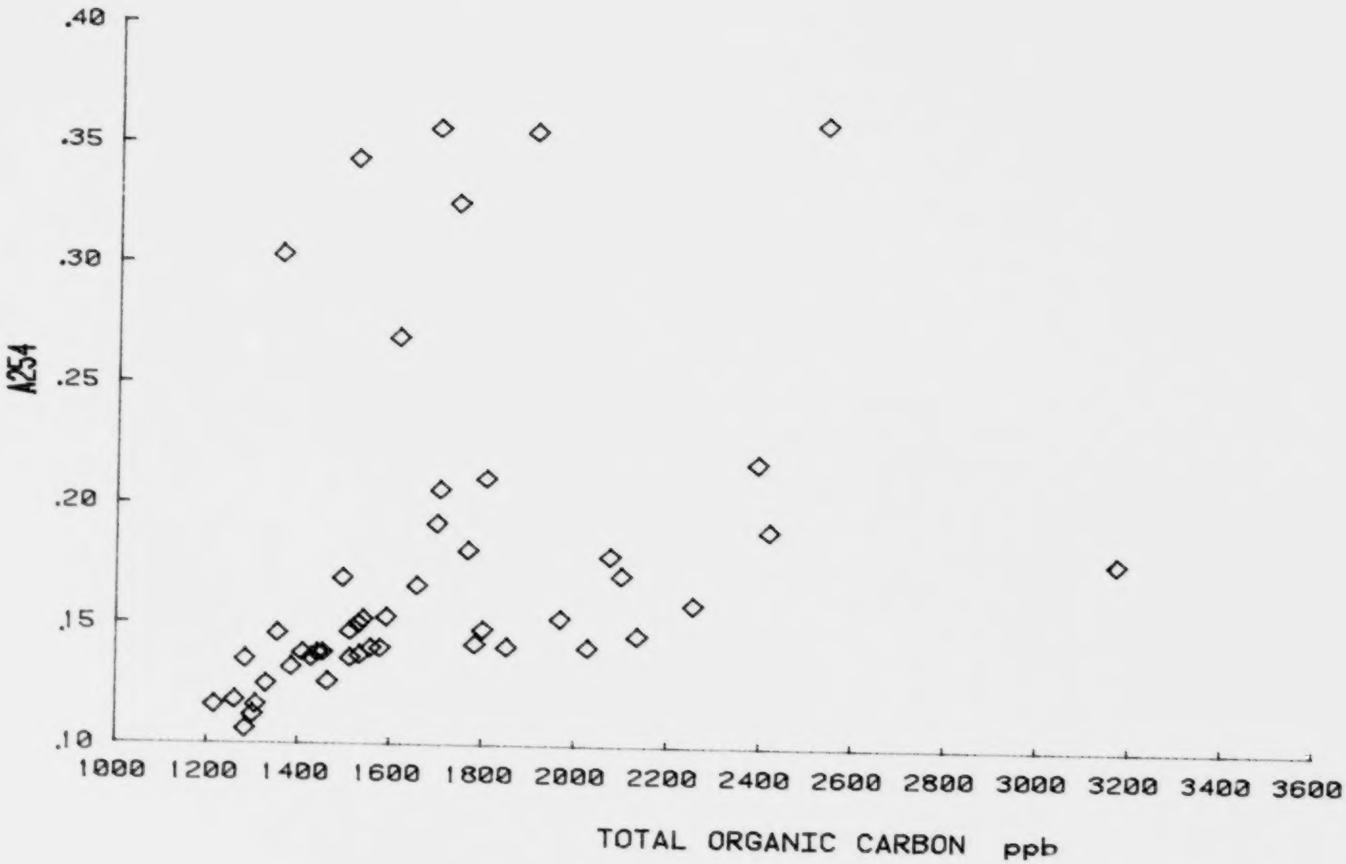

Figure 149. TOC vs. A254 - Influent to Mini-Columns.

experiments even though good reproducibility was demonstrated between contactors for this parameter.

Figure 150 shows the results for dissolved oxygen removal across a carbon contactor for the first 90 days. These data show the high initial demand which levels off after a few days. Dissolved oxygen was the only parameter to whow an effect of temperature differential during the initial 11 weeks of this study. Markedly less dissolved oxygen is removed by the cold contactor compared to the warm contactor.

Dissolved oxygen measurements presented a problem during the initial stages of lowered temperature operation. Samples for dissolved oxygen were collected in 300 ml BOD bottles and stored in glass stoppered bottles with a water seal until analysis. Samples were collected simultaneously and storage lasted for less than an hour. Care was taken to collect samples with minimal turbulence so that oxygen from the surrounding atmosphere would not dissolve. After the onset of the ambient-chilled mode, samples were collected from both the warm and cold influent lines to determine the effect of the lowered temperature. Data are shown in Table 72 for the warm and cold column influents.

The observed difference shown in Table 72 may have resulted from 1) altered electrode response due to temperature differential or 2) solution of atmospheric oxygen during sample collection. In order to test the first potential source of error, samples were warmed up prior to analysis. This was accomplished by placing the samples in a basin of water from the backwash tanks. This was started on 8/13/80 as shown on the table, and did not bring the two influent values in close agreement. The second potential source of error was tested by allowing the samples to overflow in place until the volume of the BOD bottle had been replaced three times. This technique was employed starting on 10/6/80 and resulted in differences in the two influents of 0.1 mg/l or less. This method of overflowing was adopted for all subsequent samples.

The occurrence of solution of atmospheric oxygen into the samples makes interpretation of the dissolved oxygen data difficult during the initial stage of the ambient-chilled mode of operation as no control was available for the column effluent. Thus, all comparisons in the following discussion deal with dissolved oxygen measurements at ambient temperature or after the adoption of the overflowing technique. However, the differential between the warm and cold influents (mean = 0.24 ± 0.11, mg/l) indicates that sampling error was not responsible for the 1 to 2 mg/l differential observed between warm and cold effluents. Furthermore, this temperature induced DO differential continued in later experiments in which a technique with less sampling error (mean error = 0.07 ± 0.03, mg/l) was used.

The results of the Warburg respirometric analysis on GAC taken from contactors 1 through 5 are shown on Figure 151 for oxygen uptake on the ambient contactor. Figure 152 shows the results of Warburg respirometry and biometer techniques for carbon dioxide evolution from core samples taken from contactors 1 through 5. The average oxygen uptake per gram of carbon as

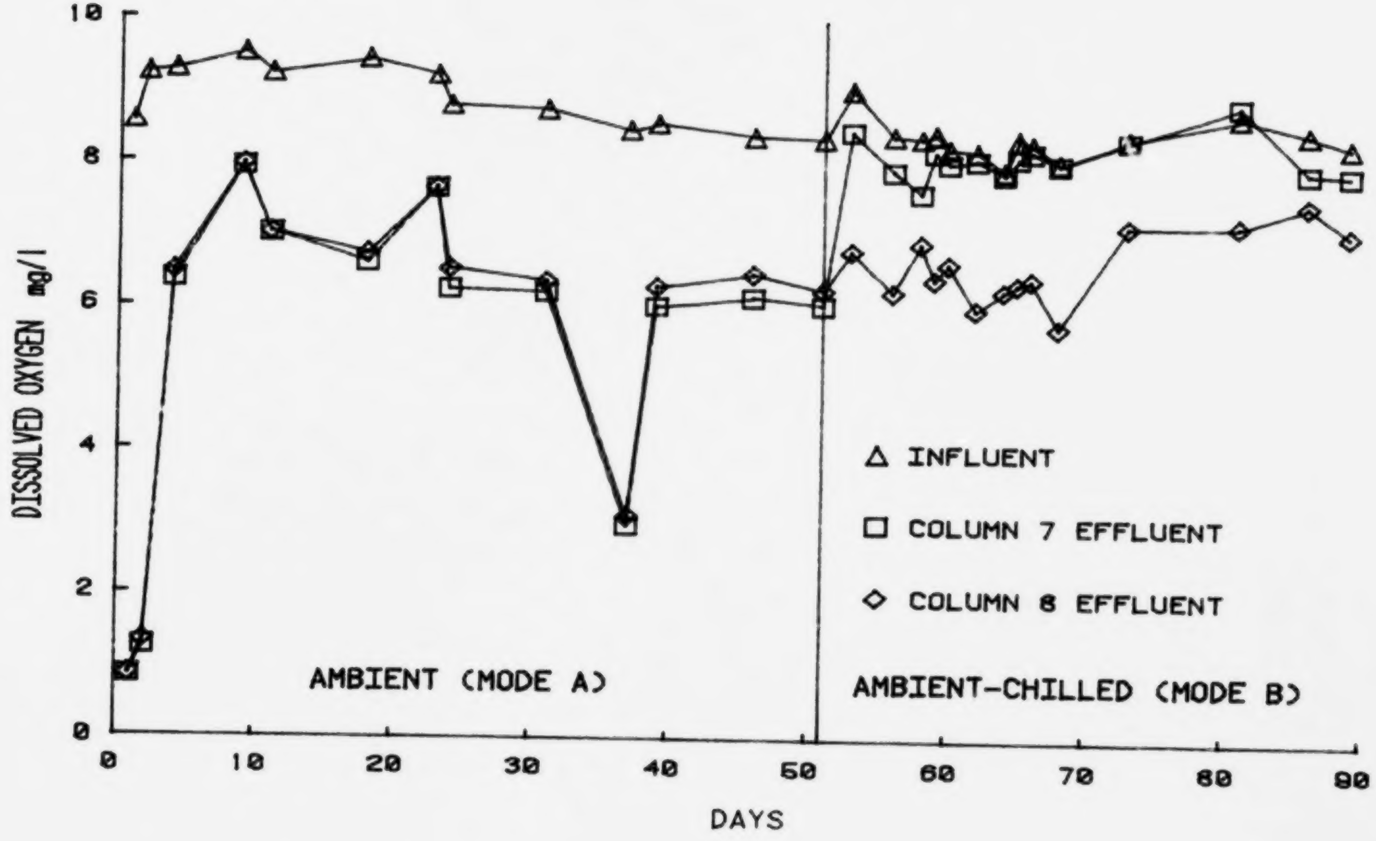

Figure 150. DO profile across GAC contactor (Reproducibility Study Modes A & B).

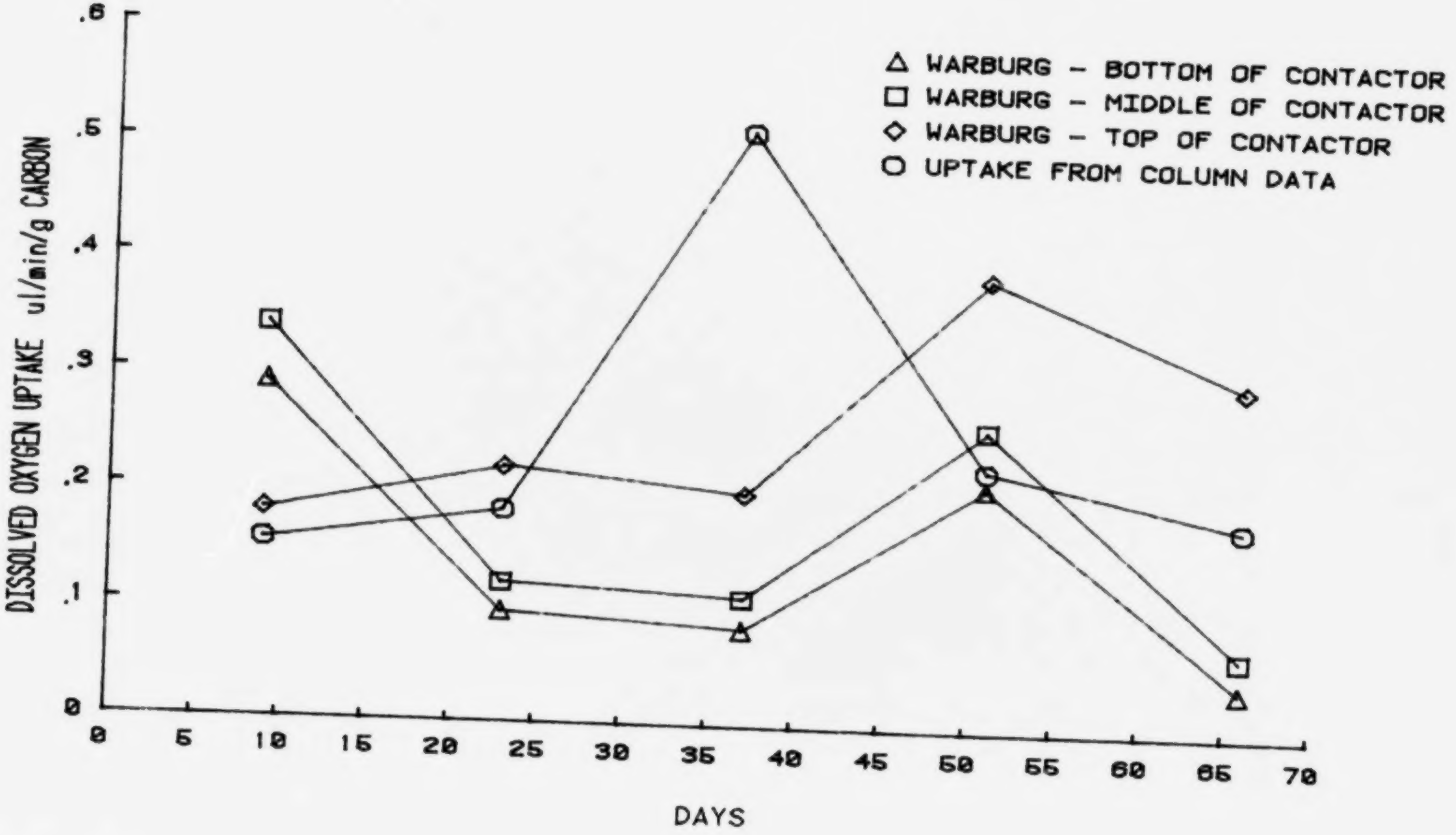

Figure 151. Warburg oxygen uptake by bacteria (core samples from contactors).

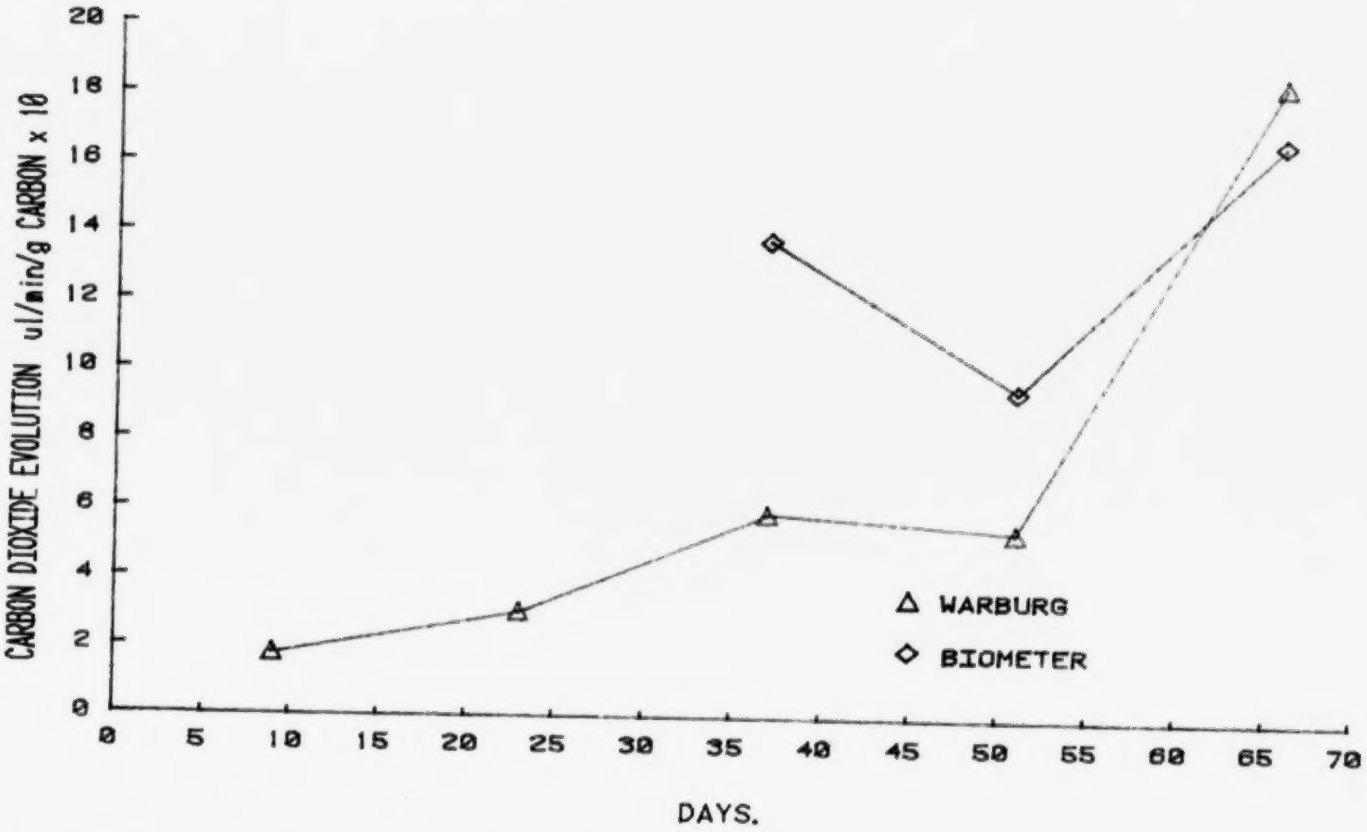

Figure 152. Respirometric carbon dioxide evolution by bacteria (core samples from contactors).

TABLE 72. DISSOLVED OXYGEN MEASUREMENTS
EFFECT OF TEMPERATURE DIFFERENTIAL

	Date	Dissolved Oxygen mg/l		
		Warm	Cold	Difference
	08/09/80	8.11	7.93	0.18
(1)	08/13/80	8.66	8.39	0.27
	08/21/80	8.87	8.43	0.44
	08/26/80	8.50	8.48	0.02
	08/29/80	8.30	8.16	0.14
	09/02/80	8.33	8.04	0.29
	09/05/80	8.52	8.16	0.36
	09/09/80	9.51	9.23	0.28
	09/12/80	8.52	8.31	0.21
	09/13/80	8.72	8.25	0.47
	09/16/80	8.75	8.53	0.22
	09/17/80	8.55	8.33	0.22
	09/20/80	8.74	8.58	0.16
	09/23/80	8.53	8.29	0.24
	09/26/80	8.70	8.52	0.18
	09/26/80	6.84	6.63	0.21
(2)	10/06/80	9.60	9.50	0.10
	10/13/80	10.09	10.05	0.04
	10/20/80	10.00	9.92	0.08
	10/27/80	10.35	10.25	0.10
	11/05/80	10.76	10.72	0.04
	11/10/80	10.63	10.57	0.06

(1) Samples warmed in water bath.
(2) Samples collected by overflowing by three sample volumes.

determined from the drop in oxygen across the GAC contactor just before it was taken offline is also plotted in Figure 151, to compare with the average oxygen consumption from Warburg analysis of three locations in the contactor (top, middle and bottom sections). The Warburg data is on the same order of magnitude as the contactor data, but does not follow the same pattern. The analysis of the entire study shows that these data (Warburg and biometer) were collected prior to the breakthrough curve reaching 50% of the steady state removal (i.e. at effluent/influent <0.3, see discussion). For this reason, these data will not be used in assessing bacterial contributions to long term TOC removal, but are included to provide a base of data for any future work.

Bacterial densities as determined by modified plate count are shown for the ozone retention tank, mini column influent, and effluents from contactors 7 and 8 on Figure 153. The effluents do not show an effect of temperature. A major difference between the data in this study and previous investigations

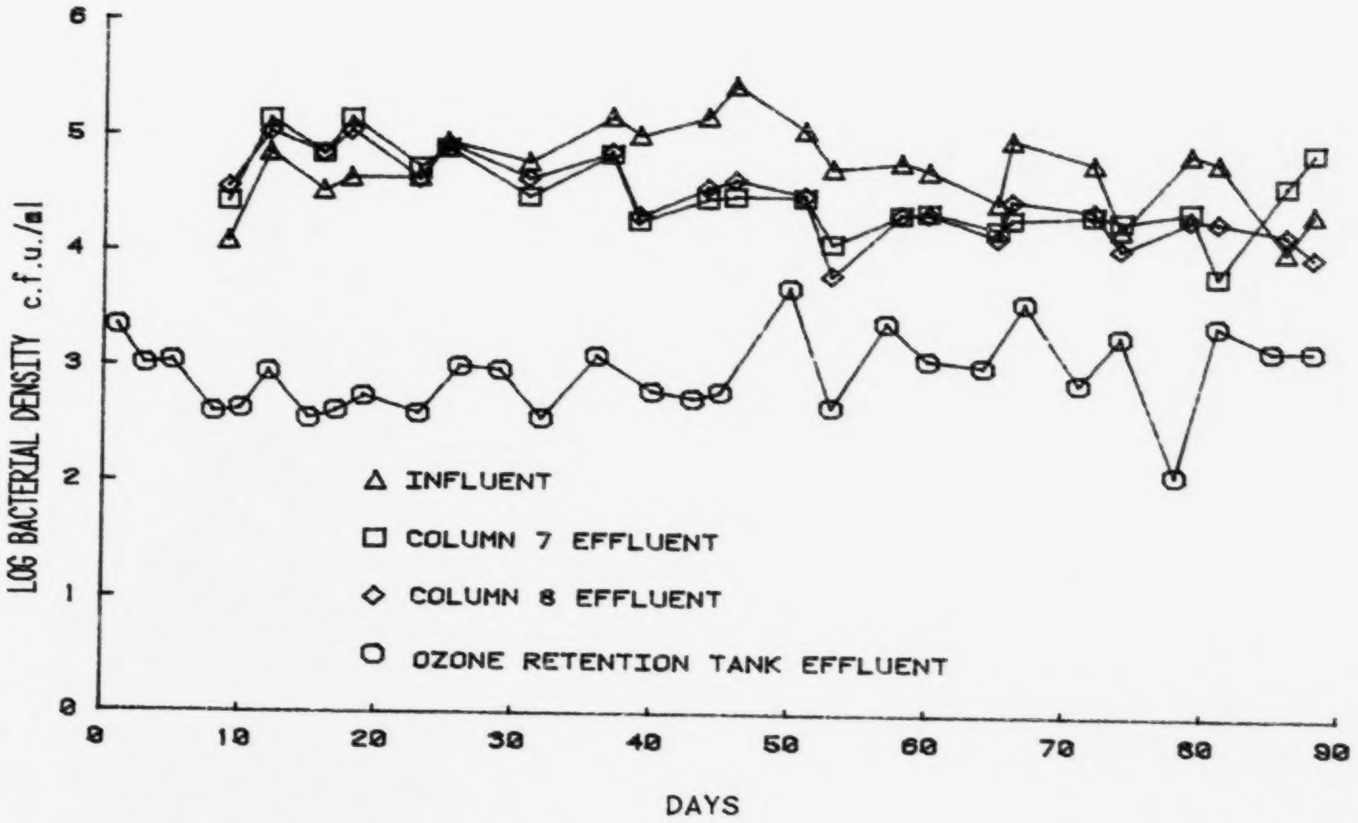

Figure 153. Bacterial densities in water (Mini-column influent and effluent-Reproducibility Study).

(116,118) is the presence of high bacterial densities in the influent to the carbon contactor. This leads to a net loss of bacteria across the contactor during some sampling periods.

Most GAC studies in the United States have been conducted on water supplies in which the bacterial density has been suppressed through the use of chlorine as a disinfectant. The number of bacteria in the effluent from a carbon contactor has been used as an indication of the level of bacterial activity in GAC contactors (116,118,120). The high numbers of bacteria in the influent for this study (relative to previous GAC work) are presumed to occur due to a combination of the following four factors:

1) the absence of disinfecting residual
2) increased substrate formation due to ozonation
3) surface area in the sand prefilter (EBCT = 1 min)
4) surface area in the 30 feet of connecting line from the ozone retention tank in the pilot plant to the small scale contactors

Regardless of the individual contributions of each of the above factors, a comparison of the bacterial densities and TOC in the ozone retention tank (influent to sand prefilter) and small scale contactor influent (effluent from the sand prefilter) will show the effect of large bacterial density increases on TOC concentrations. Figure 154 shows the TOC concentrations before and after the sand prefilter during this portion of the study. Figure 153 showed the bacterial densities in the same locations. Although there is a consistent difference in the bacterial densities of approximately two orders of magnitude, the TOC data do not show the consistent difference. Therefore, it appears that large increases (i.e. two orders of magnitude) in bacterial density are not a good measure of TOC reduction at dilute concentrations (1.2 to 1.7 mg/l TOC).

The temperature control through the various modes of operation was presented in Table 13. Three modes of operation were employed while the adsorption unit process exhibited no effect of temperature. These were ambient (Mode A), ambient-chilled (Mode B) and the first portion of warmed-ambient (Mode C) up to approximately day 250. This demonstrates that the hypothesis that temperature has a negligible effect on the adsorption of TOC is acceptable. Longer term TOC removal will be discussed below.

Long Term TOC Removal

The purpose of this experiment was to demonstrate that TOC removal could be controlled by temperature once the adsorptive capacity had been exceeded. It also allows comparison with other GAC experiments as reviewed by Roberts and Summers (41) in terms of the characteristics of the Philadelphia project with respect to projects elsewhere in the world.

Two of the contactors (columns 7 and 8) from the reproducibility experiment were maintained on line to test the contribution of bacteria to long term TOC removal. Previous investigators (113) have postulated that the initial action of GAC as a unit process is adsorption, but changes to purely biological after a certain time (1 to 3 months). The lag in temperature

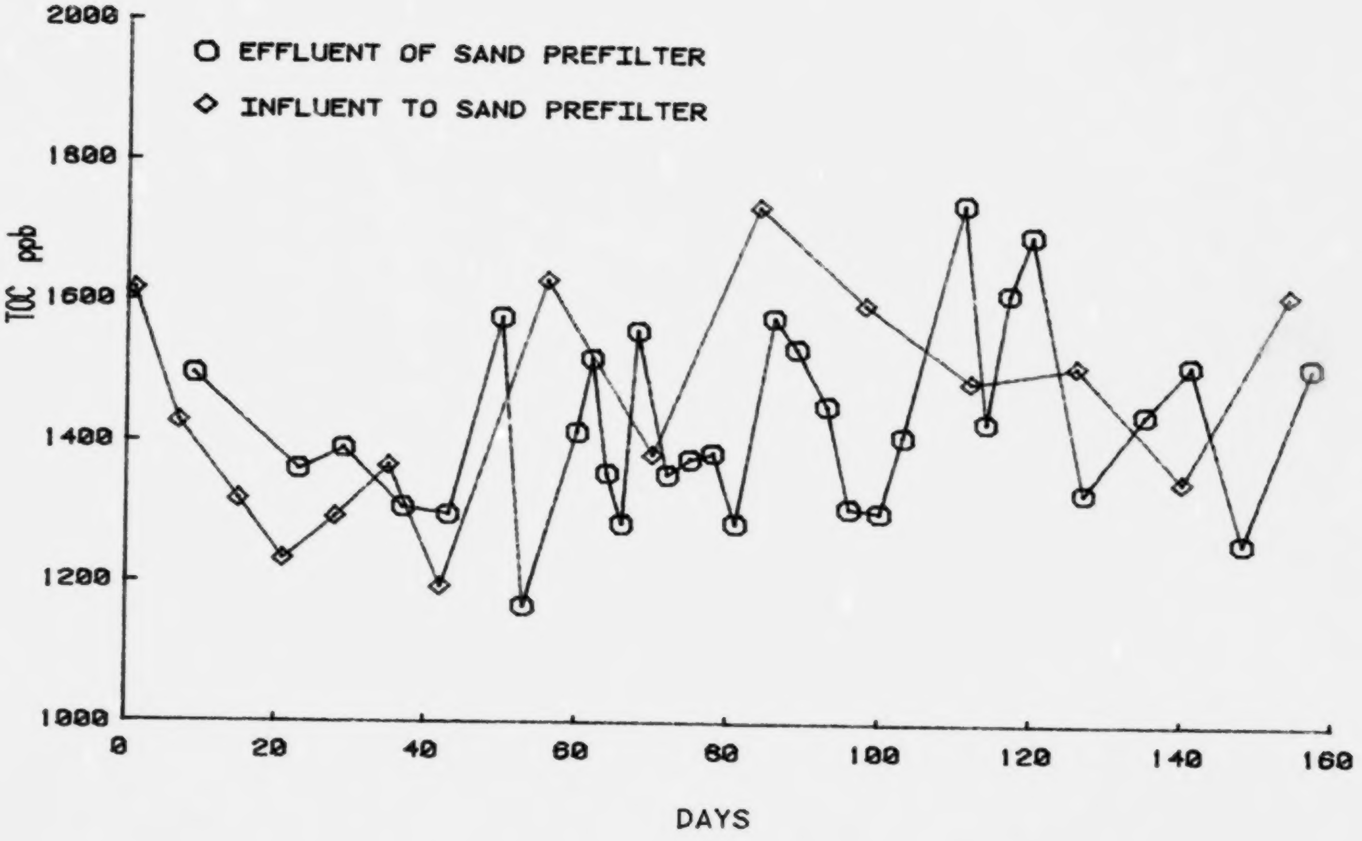

Figure 154. TOC profile across sand prefilter from ozone retention tank to small scale contactors.

induced TOC differential has also been reported elsewhere (44). Figure 155 shows the TOC profile across the warm and cold GAC contactors for the first three modes of operation (A, B, and C, see Table 13). Note that after day 250, up to the end of Mode C (Day 325), the effluents of the warm and cold GAC contactor no longer followed the same pattern and a temperature induced TOC differential was observed.

The interplay of TOC and DO removal around Day 250 suggested one or both of two mechanisms which could explain the TOC removal differential:

1) the bacteria on the warm contactor GAC were regenerating the surface and metabolizing adsorbed biodegradable TOC. This explanation is an interpretation of the "BAC" theory (118) in which bacteria are able to use adsorbed substrate.

2) the temperature change had induced a shift in equilibrium on the GAC that allowed previously adsorbed biodegradable material to desorb into the aqueous phase where bacteria were able to use it. This explanation assumes that organic substrate must be in the aqueous phase, i.e., not adsorbed, for bacteria to use it.

The dissolved oxygen data are shown on Figure 156 for the first three modes of operation. Note that the removal on the warm contactor increased dramatically upon changing the mode of operation from ambient-chilled to warmed-ambient. This high removal was maintained until about Day 250, when it began to drop off to a level greater than that observed during mode A, but much less than at the onset of Mode C.

The interpretation of the "BAC" process (112) used to explain the high dissolved oxygen demand preceding the TOC removal differential is as follows. A mechanism for the temperature induced TOC removal differential was proposed in which more rapid regeneration of the carbons' surface in the warmer contactor (due to warmth accelerated bioactivity) may have created more adsorptive capacity on the warm contactor than on the cold contactor. In this mechanism, it is hypothesized that the GAC is storing (through adsorption) biodegradable materials because there are insufficient bacteria to mineralize the material. The potential sources of the biodegradable material, particularly by acclimization to recalcitrant substrates (27) will be addressed in the discussion. When the temperature was suddenly increased, bacteria acted much more rapidly, thus the high oxygen demand. The high demand subsided when most of the biodegradable material adsorbed on the GAC had been mineralized. The more rapid rate on the warm contactor is hypothesized to have regenerated the surface faster, allowing the TOC differential to occur.

The possibility that the differential TOC removal was due to a regeneration of the carbons surface rather than a reduction in the rate of biodegradation in the cold contactor led to the following changes in mode of operation. These changes were implemented to test the applicability of the experimental method. The effects of a more rapid regeneration of the GAC's surface on the warm contactor and the interpretation in light of parallel data from the pilot scale contactors will be discussed in detail later.

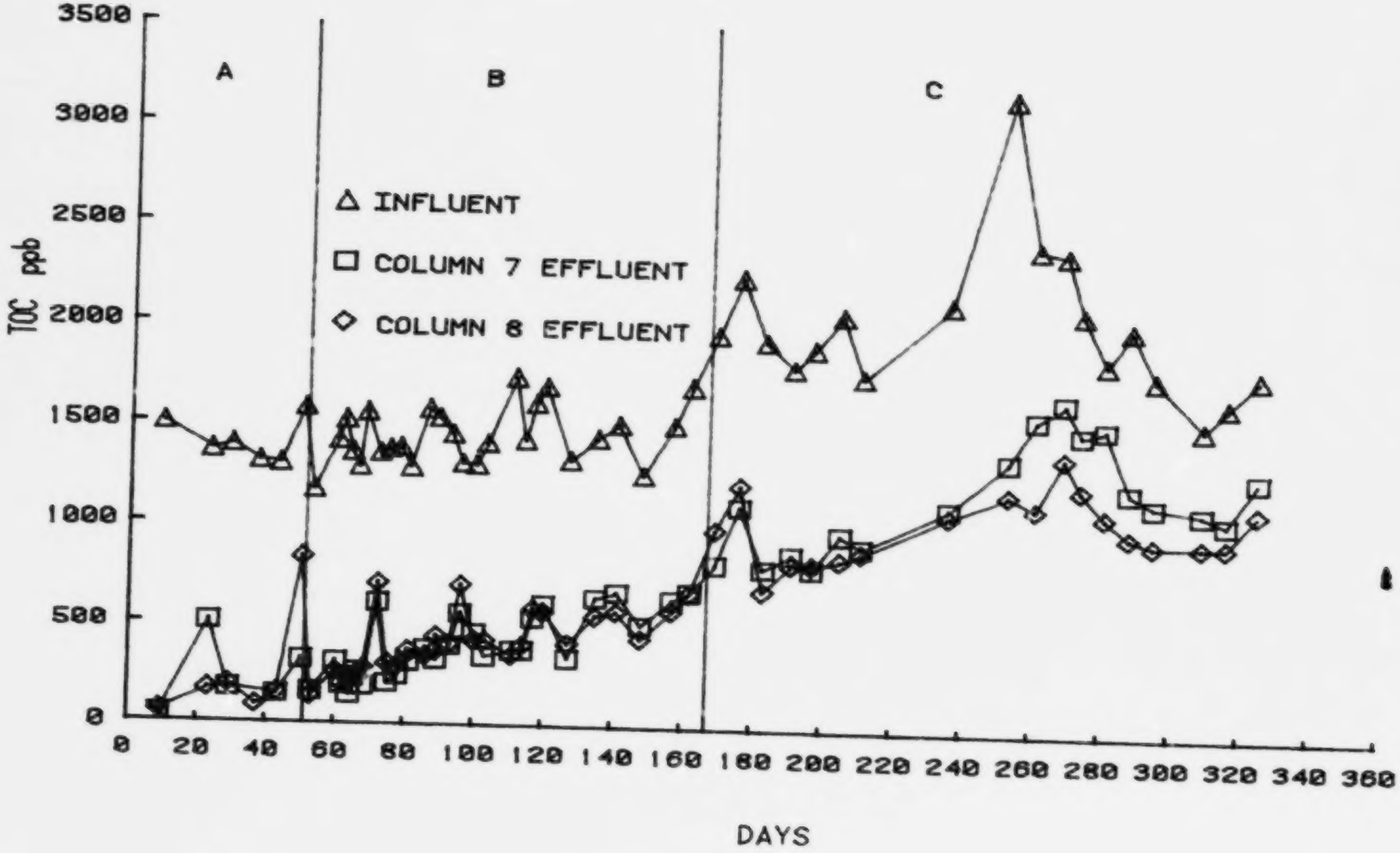

Figure 155. TOC profile across GAC contactor (warm and cold - Modes A to C).

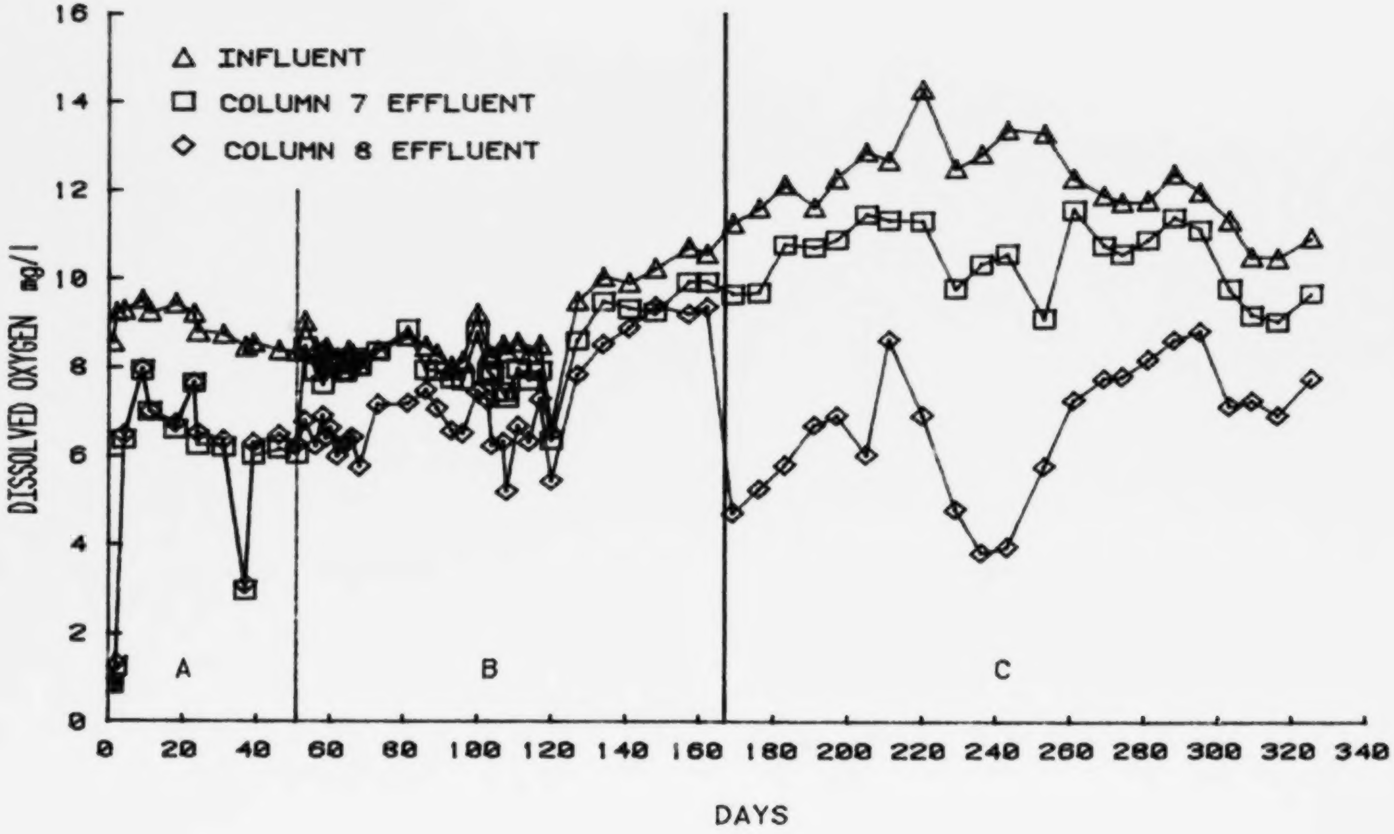

Figure 156. DO profile across GAC contactor (warm and cold - Modes A to C).

The temperature on the cold contactor was increased on Day 325 to attempt to duplicate the large DO demand and subsequent TOC removal dfferential without the aid of a temperature differential. In this manner, the temperature induced shift in equilibrium would occur on the former cold contactor, but should not be reflected in the warm contactor as the high DO demand had already been induced, and had apparently declined by about Day 250. Figure 157 shows the DO profile across the two contactors during the warmed-warmed mode of operation and a subsequent ambient mode (D and E). The large DO demand was not duplicated and a TOC differential was not induced (see Figure 158 for TOC). Therefore a test of the "BAC" mechanism (regeneration of the GAC surface) did not produce the expected results and the theory is rejected as a mechanism operating in this study.

Bacterial Growth Study

This study was an extension of the mini column work using parallel GAC contactors to those used for long term removal studies. The purpose was to observe growth rates on contactors receiving different influent bacterial densities. During the bacterial loading study, only plate counts were monitored. Figure 159 shows the influent and effluent bacterial densities on a logarithmic scale. Figure 160 shows the influents only on a linear scale to emphasize the reduction in bacterial densities. Figure 161 shows the bacterial densities on the GAC. Note the lag in bacterial buildup on carbon receiving filtered water.

TOC Removal Rate

The purpose of this experiment was to determine the rate of biological TOC removal on sand as compared to GAC. This determines the applicability of sand as an estimator of bioactivity on GAC. Once the rates of removal on sand and GAC are demonstrated to be comparable, the relative contributions of biodegradation and slow adsorption can be determined.

This experiment was conducted at the end of the pilot study with the two carbon contactors remaining from the adsorption reproducibility study plus two newer sand contactors of equal EBCT. The purpose was to measure the effect of temperature on the rates of TOC removal on sand and GAC and to demonstrate that the TOC removal differental established at the end of Mode C (days 260 to 320) was related primarily to temperature and could be reestablished by a return to the ambient-chilled mode of operation.

Figure 162 shows the effect of temperature differential on DO demand across a carbon contactor. The differential demand was re-established immediately upon returing to the ambient-chilled mode. The demand exerted by the warm and cold sand contactors is much less than the carbon's demand. The lower demand for DO and efficiency of bacterial acclimization to the environment because the cold sand contactor has been on line (at ambient temperatures) for 146 days at the onset of Mode F, and the warm sand contactor had been on line (at ambient temperatures) for over 200 days.

Figure 163 shows the TOC profile across the sand and GAC contactors during Mode F. Note that the general trend in effluent TOC removal:

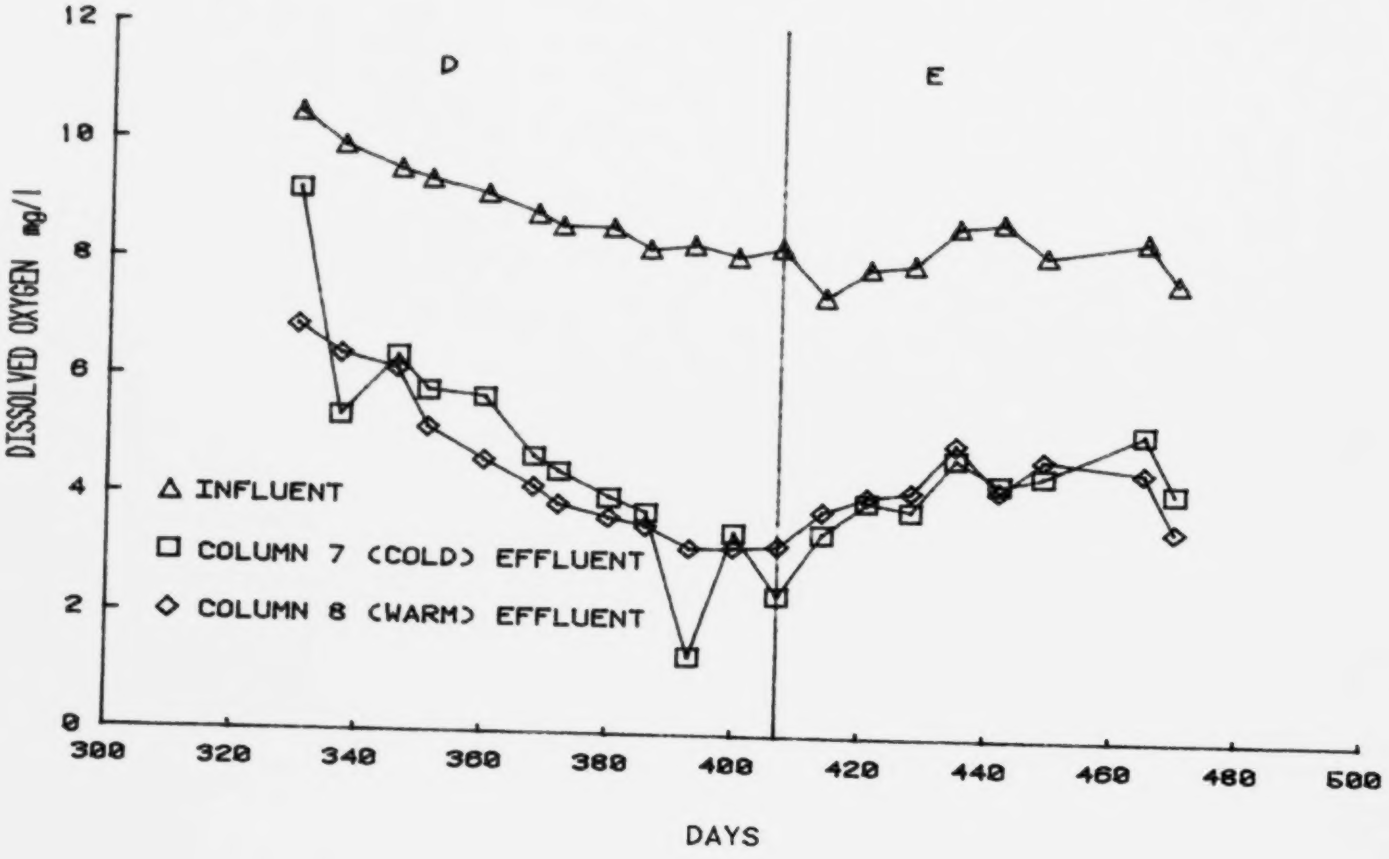

Figure 157. DO profile across GAC contactor (warm and cold - Modes D and E).

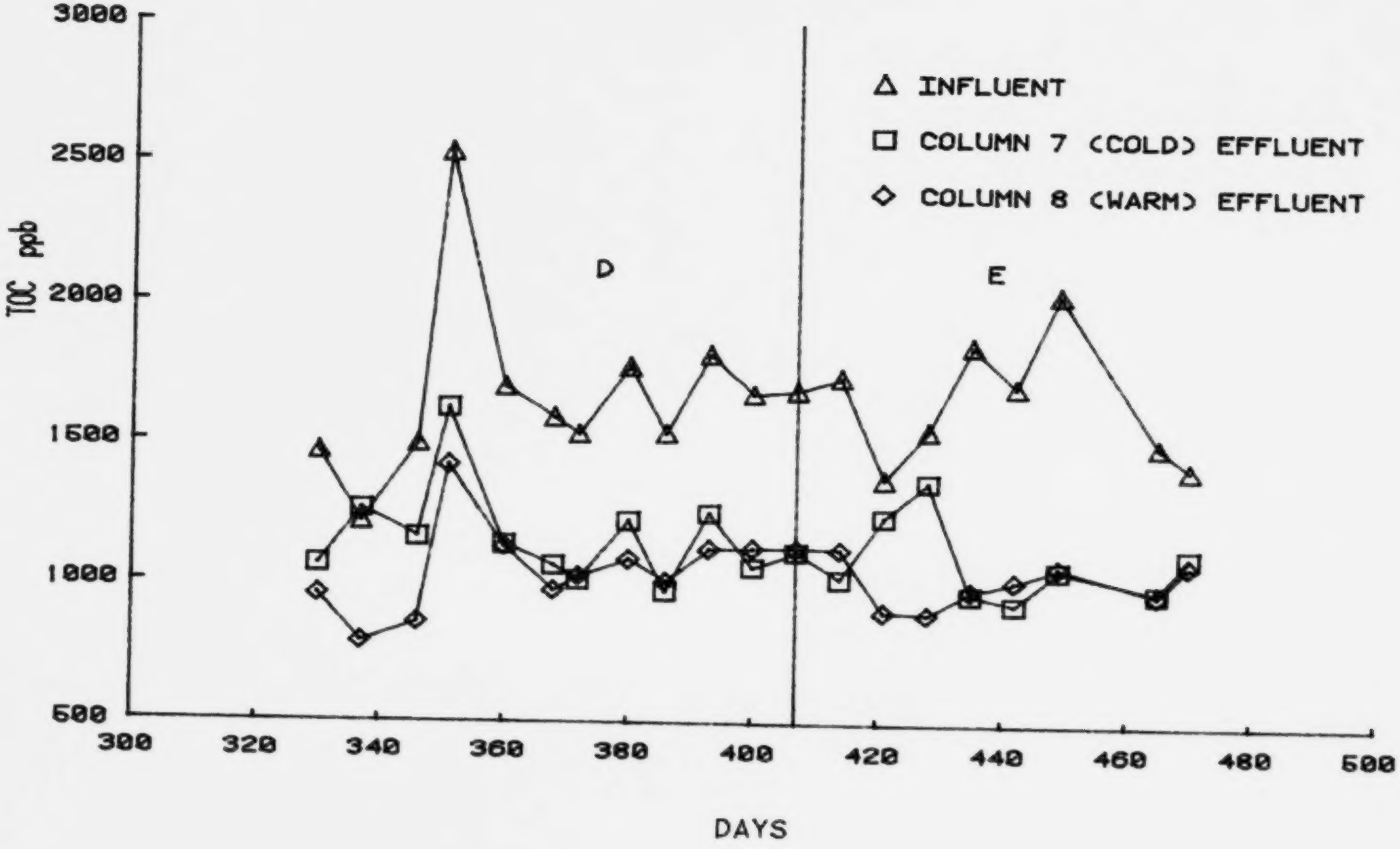

Figure 158. TOC profile across GAC contactor (warm and cold - Modes D and E).

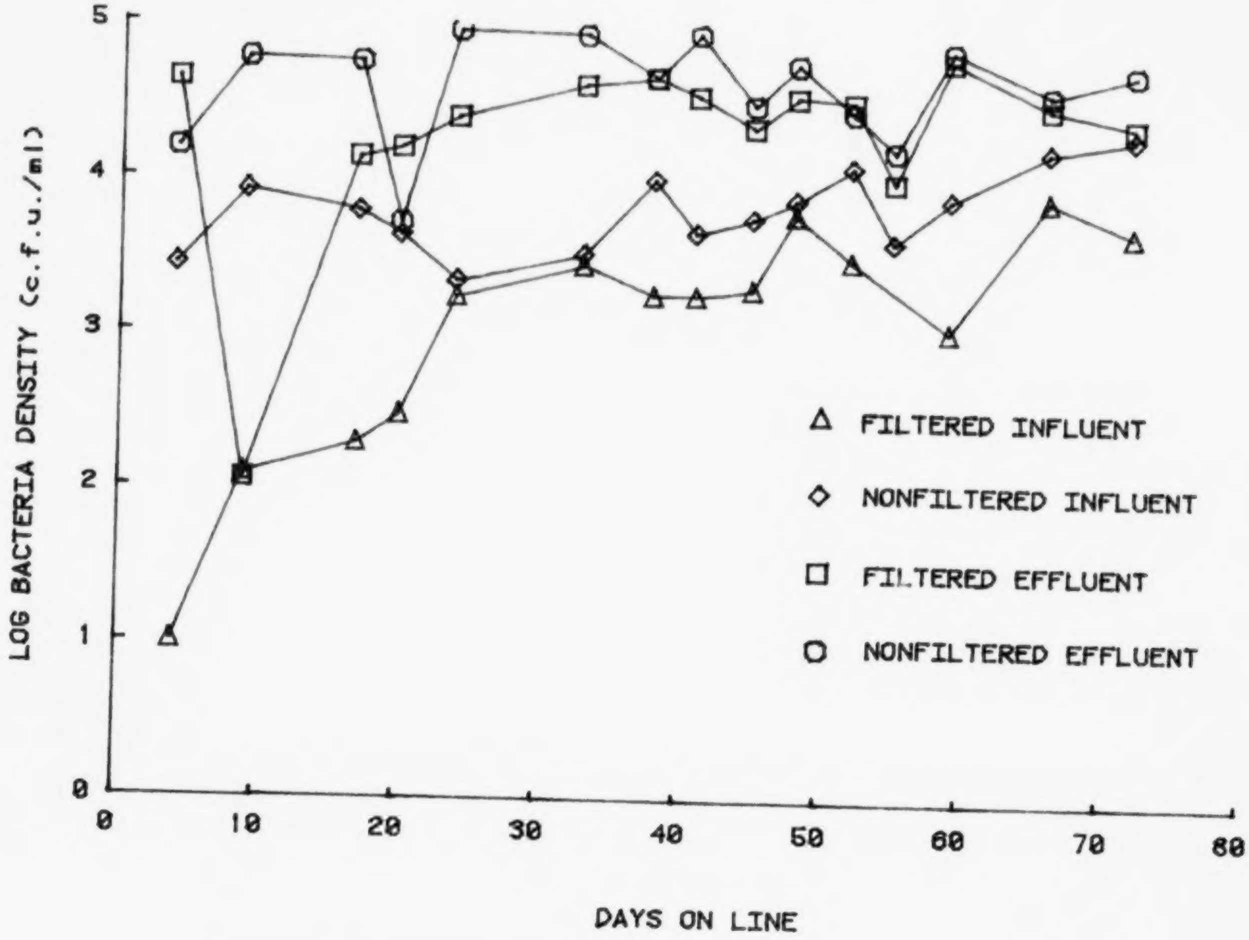

Figure 159. Bacterial densities in water - Growth Study - Log.

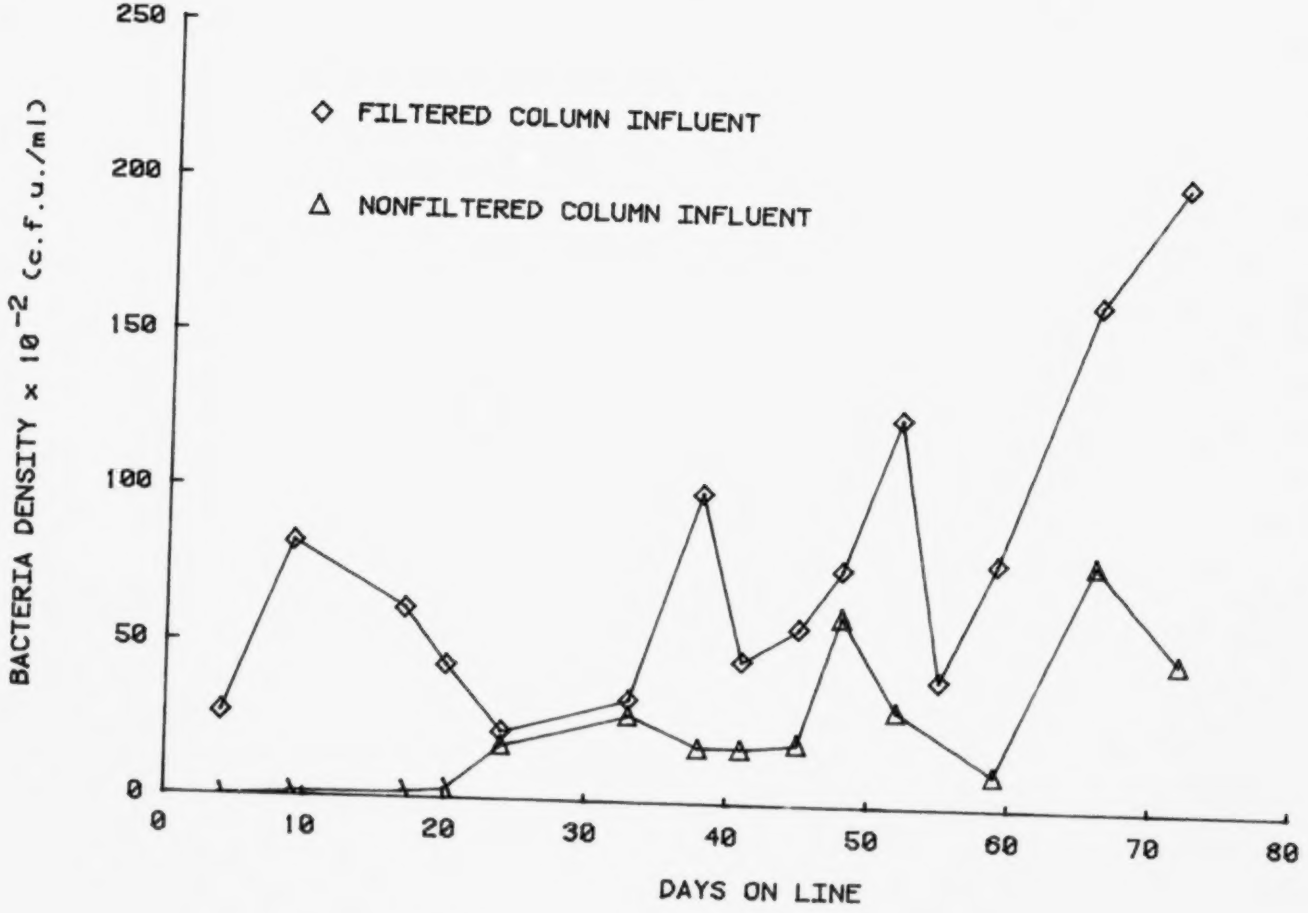

Figure 160. Bacterial densities in water - Growth Study - Linear.

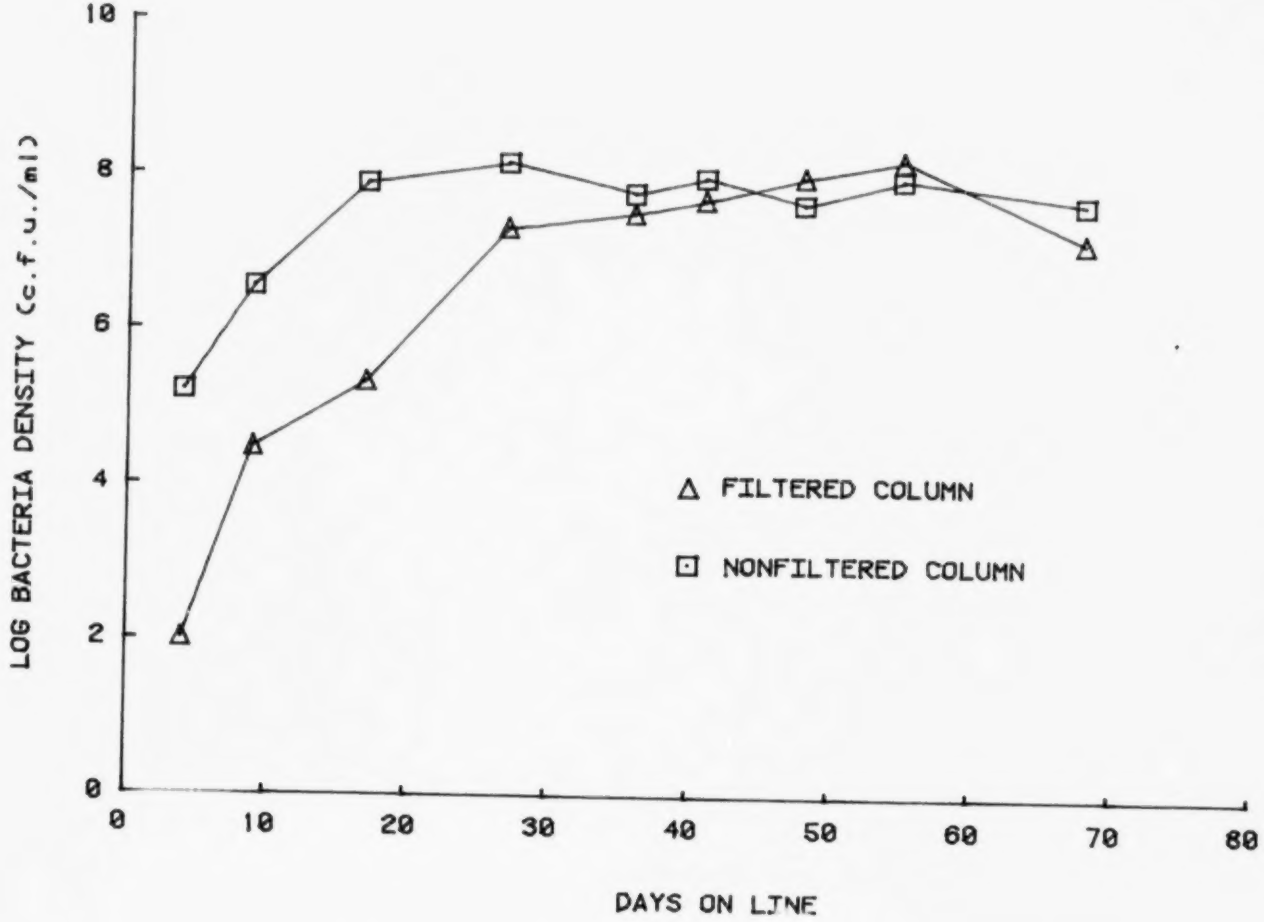

Figure 161.- Bacterial densities on GAC - Growth Study.

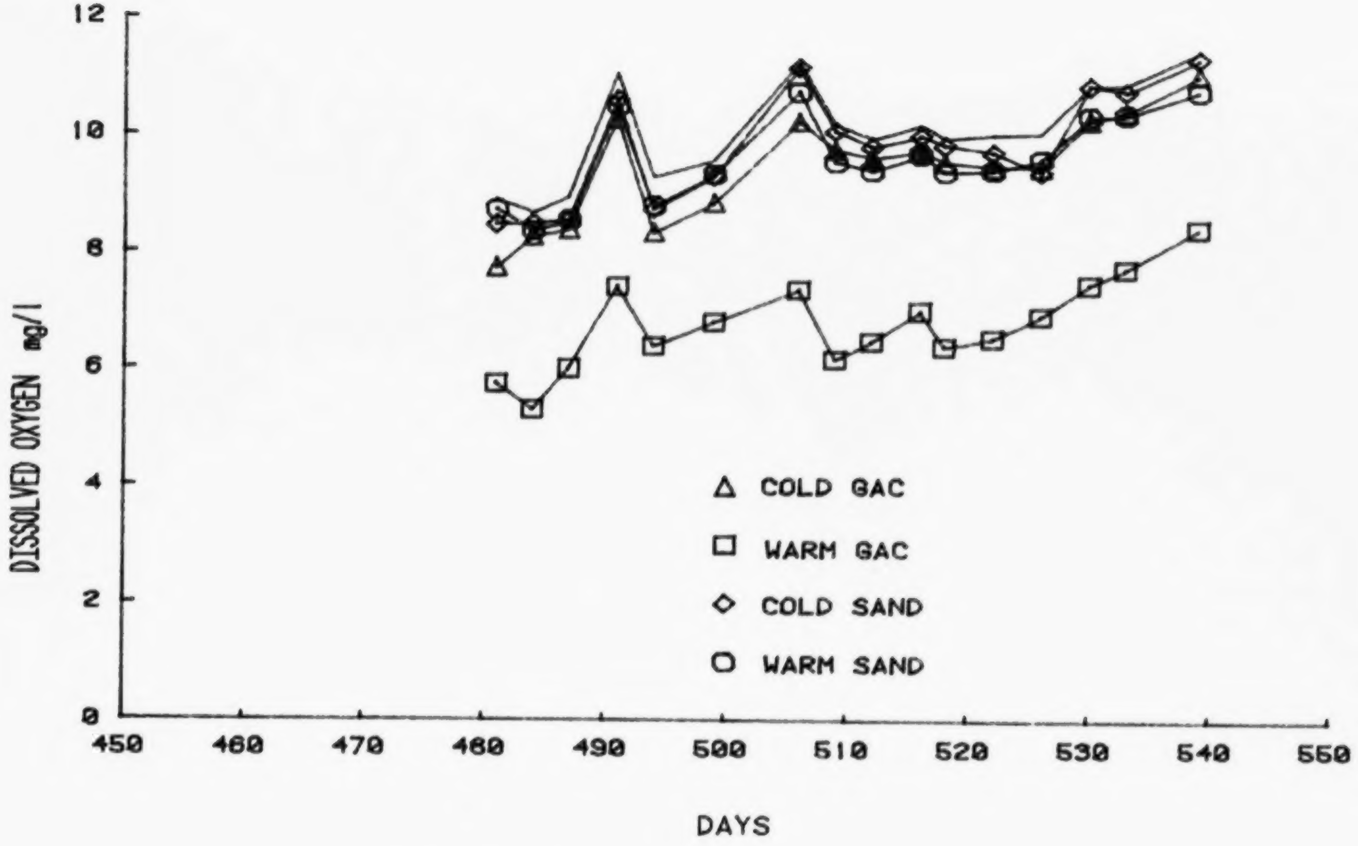

Figure 162. DO profile across sand and GAC (Rate Study).

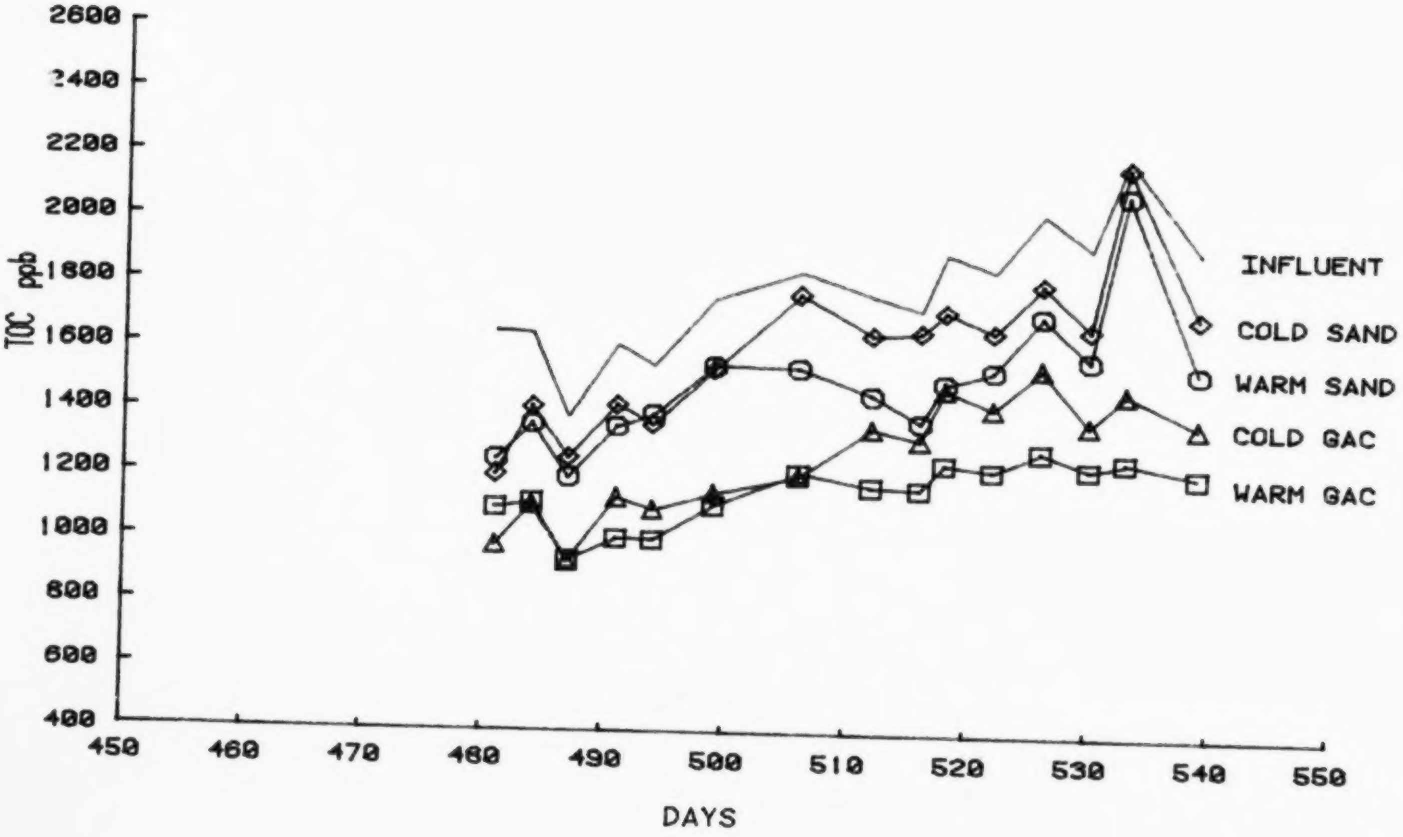

Figure 163. TOC profile across sand and GAC (Rate Study).

Warm GAC > Cold GAC > Warm sand > Cold sand

The early portion of Mode F was plagued by temperature control problems in the operation of the cooling bath. Although a temperature differential of 10 degrees centigrade or greater was maintained, the cold contactor was not below 7 degrees consistently as was the case in the later part of the study. It appears that the low level of biodegradable materials can be removed by bacteria as long as the temperature is above approximately 7 degrees centigrade. This was also demonstrated in pilot plant sand contactors using the same raw water. In that case, all TOC removal observed on sand occurred in the first of two sand contactors in series, each of which a 15 minute empty bed contact time.

For these reasons, it appears more important to control the low temperature in this type of study than to have a large temperature differential (i.e. > 10 degrees centigrade).

SECTION 8

DISCUSSION

INTRODUCTION

This study was conducted to investigate the technical and economic feasibility of incorporating an ozonation and/or GAC unit process into a conventional water treatment train for the purpose of removing trace organic substances of health concern. The relationship between adsorption and biological activity during water treatment with ozone and GAC was carefully evaluated. The primary concern for the practical use of GAC is lowering its operating costs by increasing its useful bed life. To achieve this objective the removal of trace organic substances of health concern at the ng/l to ug/l level and the removal of TOC at the mg/l level were carefully monitored along with microbial parameters of biological speciation and growth rates. The frame of reference for this study has been previously described (Figure 1) as design elements for the Carbon Adsorption Process (1). The engineering evaluation and economic analysis derived from the biological and chemical considerations of nonspecific, specific and screening protocols are evaluated in terms of health effect priorities (Table 1).

GAC systems have been shown to be both technically feasible and operationally manageable at Philadephia's Torresdale WTP, but a severe economic burden on the water utility would be apparent, based upon a 3-month regeneration cycle (2). This short regeneration cycle will be necessary if the GAC is to remove the trace levels of organics presently found in the Torresdale Plant rapid sand filter effluent (Figure 164). In addition, another concern is to maintain the disinfection of the drinking water while reducing organic compounds of health concern. Therefore, three general considerations are addressed in this study:

1. An understanding of how ozonation, as a pretreatment to GAC adsorption, can increase the useful bedlife of the GAC sufficiently to justify the cost of ozonation.
2. An understanding of how to enhance TOC removal prior to GAC treatment in order to increase the capacity of GAC for the removal of trace organics of health concern and organoleptic compounds.
3. An understanding of how disinfection in the distribution system can be properly maintained with post GAC chlorination after conventional treatment with and without preozonation and/or prechlorination.

The interpretation of the results of this study was aided by evaluation

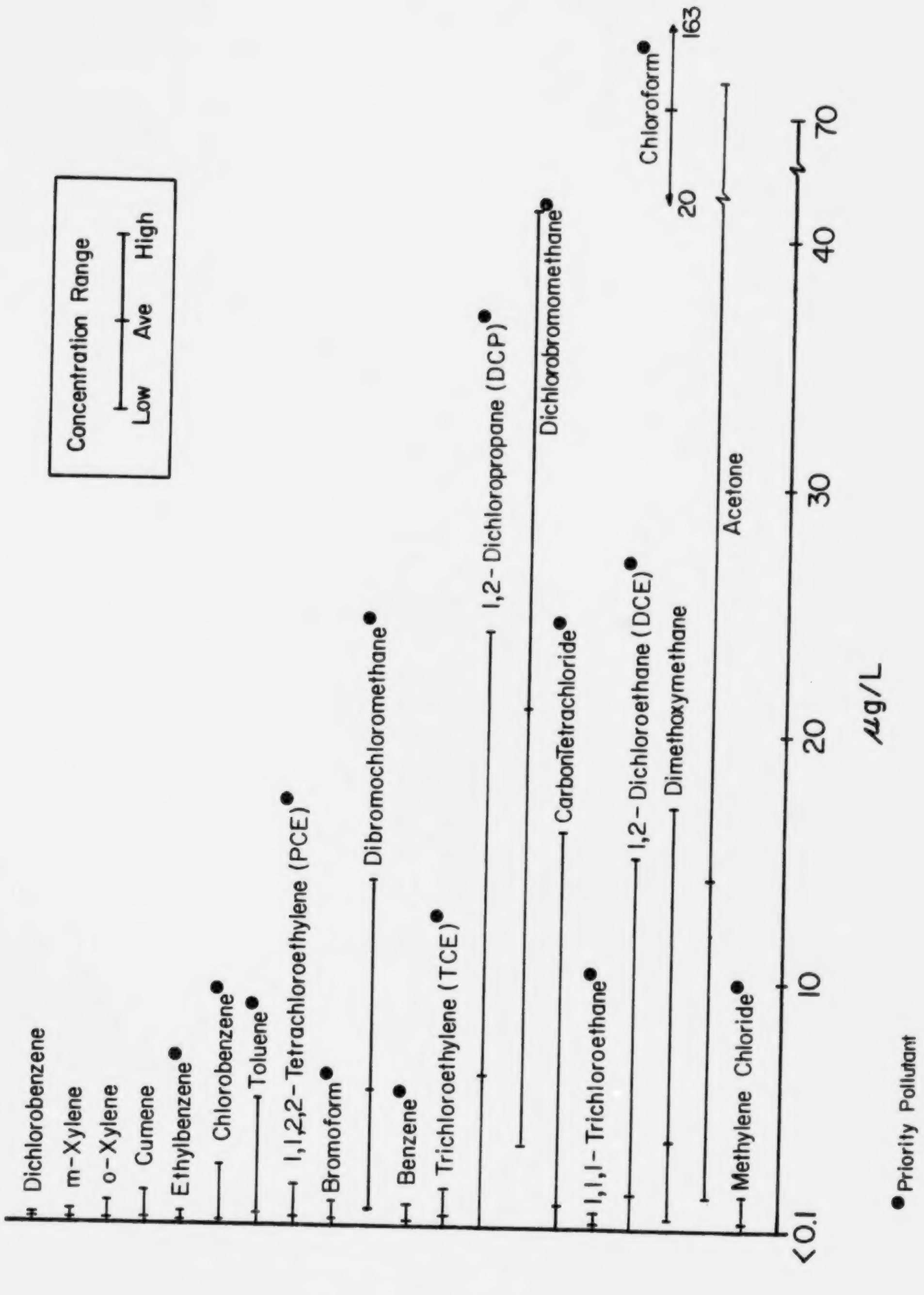

Figure 164. Volatile Organic Analyses - Torresdale effluent (4/80 to 4/81).

tools developed by laboratory and pilot scale ozonation studies, mini-column GAC studies and pilot plant data on sand contactors. The most important of these techniques are:

1. Laboratory investigation into understanding and operating the ozonation process using ozone utilized, UV and TOC kinetics, and measuring ozone in the presence of aqueous chlorine.
2. Laboratory and pilot scale investigations of the simultaneous unit operations of aeration and oxidation to enable an understanding of the relationship between them.
3. Pilot Plant results that verify that bacterial TOC removal (of products of ozonation) through a sand bed of EBCT = 15 minutes is essentially complete. Therefore, sand beds can be used to judge the effectiveness of ozonation for producing biodegradable organics.
4. Minicolumn results verifying that TOC removal by biodegradation is equivalent on sand and GAC. Therefore, sand contactors of equivalent empty bed contact time could be used to judge the relative contributions of bacterial degradation and adsorption on GAC for TOC removal.
5. Replicate contactors in the minicolumn studies that demonstrate that the GAC process is very reproducible for the general and specific organic parameters (as determined by TOC and broad spectrum analyses).
6. Ozone/sand studies verifying that the effectiveness of the two ozonation systems used in the pilot scale studies were operating equivalently.
7. Laboratory investigations into optimizing the recovery of bacteria by a modified plate count technique.

LABORATORY OZONATION STUDIES

The objective of the laboratory ozone studies was to develop an understanding of the ozone process for drinking water. The specific ozone studies included investigations into the ozonation of Delaware River water, the concept of ozone utilized, and ozone kinetics. This information was included in the development of a laboratory protocol for ozonation systems which could be used to observe the effect of ozone treatment prior to large scale operations.

Development of Ozonation System Test Protocols

The objectives of this research include an examination of the viability of ozonation as a potable water treatment process especially for removal of micropollutants and oxidation of humic substances. In order to implement this, a protocol for laboratory testing of an ozonation system prior to large scale operation has been devised. This consists of a systematic method for experimentally determining or deriving the operational parameters necessary before designing a potable water treatment system using ozone and also allows for the continued testing (for control purposes) of an on-going ozonation process. A schematic is shown in Figure 165.

It should be recognized that this direction represents a result of this project and not an "a priori" direction. In the initial stages of the project, a review of the literature indicated that no rational design criteria existed for studying the unit process of ozonation in potable water. Specifically, parameters extremely important to the ozonation process such as mass transfer, ozone decomposition rates, stripping, substrate monitoring, etc., were not normally considered. It is hoped that future ozone studies will be able to better incorporate these concepts into their investigations as a consequence of the protocol presented here and that ozone results from different studies will be more directly comparable as a result.

The first stage of the protocol concerns the consideration of treatability. This is intended to answer the question of whether ozone will be of any use in attaining the treatment goals. In the O_3/GAC process, for example, a goal would be the production of low molecular weight biodegradable materials from high molecular weight humics in the water. This stage may be subdivided into three parts. First, criteria should be based upon the treatment goals. Second, the water quality should be examined in reference to these criteria to ascertain treatability based on properties of the system. Third, ozone should be applied to the water to confirm treatability. In the O_3/GAC process, another goal would be biological activity on carbon and the criteria would be the presence of a suitable substrate. Typical water quality parameters would be DOC or UV absorbance and 254nm (A254).

It should be kept in mind, however, that the ultimate purpose of O_3/GAC is to increse the capacity of activated carbon for removal of micropollutants. The true criteria, then, for O_3/GAC would be a comparison of carbon capacity with and without biological activity for the removal of specific pollutants. The rationale for using A254 or DOC as surrogates to determine treatability stems from the fact that it is assumed that the high molecular weight materials measured by these methods will compete with the micropollutants for sites on the carbon bed (9). By removing this source of competition through ozone treatment of the high molecular weight materials, more sites are effectively available for micropollutant adsorption, i.e. capacity is increased.

The next step in the protocol, then, is to actually determine the applicable water quality parameters. If the O_3/GAC process is being considered, this would consist of ultrafiltering a sample of the water and determining the absorbance or DOC content of the high molecular weight fractions. For purposes of this discussion, a high molecular weight would be considered to

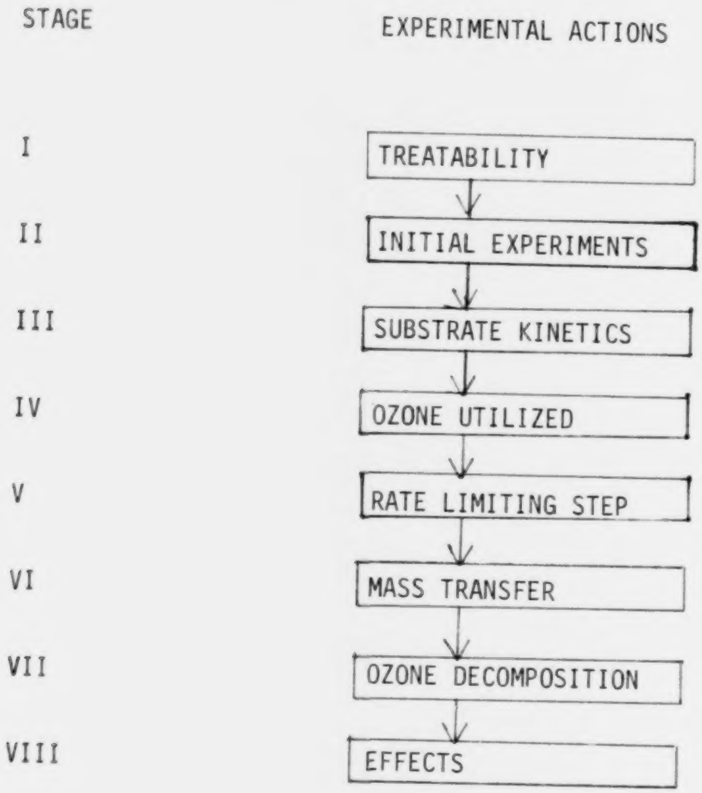
STAGE
EXPERIMENTAL ACTIONS
I
TREATABILITY
II
INITIAL EXPERIMENTS
III
SUBSTRATE KINETICS
IV
OZONE UTILIZED
V
RATE LIMITING STEP
VI
MASS TRANSFER
VII
OZONE DECOMPOSITION
VIII
EFFECTS

Figure 165. Protocol for Ozone Testing

be greater than 1000 daltons (the nominal cutoff point of a UMIO (Amincon Co) ultrafilter). A treatability index may then be defined as the product of the A254 and the percent high molecular weight material. The higher the treatability value, the greater the chance for O_3/GAC to remove high molecular weight potential competitors.

The next step is to confirm treatability. This would consist of a laboratory scale measurement to determine if ozone will indeed have the predicted impact. It may be assumed for the O_3/GAC process that a reduction of A254 implies a reduction in biorefractory potential site competitors. In the experiment, an efficient laboratory scale ozonator may be used to see the effect of ozone on the substrate after a given (although arbitrary) amount of time. The change in A254 per gram of material treated may then be used as confirmation of treatability. A schematic for the treatability section of the protocol is shown in Figure 166. Mini-column experiments used sand contactors to judge treatability, in terms of biological TOC removal, of ozonated water were proven efficient in the project.

The next phase of the protocol (Stage II) was designed to assess the effect of pretreatment on the water with regard to ozonation and to develop a monitoring technique for following the course of ozonation. This discussion should be referenced to the results of Delaware River ozonation esperiments which has been presented in detail. These results indicate that A254 is an effective monitoring technique and that pretreatment should be kept to a minimum.

The third stage of the protocol is concerned with chemical reaction kinetics of the reactions of ozone and organic substrates. By monitoring UV during ozonation of raw water or humic materials isolated from raw water as a function of time, several pieces of information are derived. These include reaction order, modality of reaction, duration of the reaction, hydraulic detention times and general rate laws for the substances being ozonated.

The fourth stage of the protocol is concerned with the optimization of ozone applied dose. Since production of ozone is very energy intensive, it is necessary to find the minimum dose that can effect a desired change if the process is to become cost effective. In the present case, this is defined as the minimun dose that can achieve UV reduction in the system by the time the ozonation break point time is reached. This may be accomplished by introducing ozone utilized as a control parameter.

In this case, the OU equation (see page 110) is rearranged as follows:

$$O_3 \text{ in} = (OU + O_3 \text{ resid})\ (Q_l/Q_g) + O_3 \text{ out}$$

Its use requires either feedback from the mass transfer portion of the protocol, or an assumption concerning the air:water ratios (Q_l/Q_g).

In the next step (Stage V) it is necessary to determine if the rate limiting step for the ozonation reaction sequence is mass transfer or reaction rate limited. This may be accomplished by performing ozone uptake experiments. If the reaction is mass transfer limited, then the mass transfer phase of the

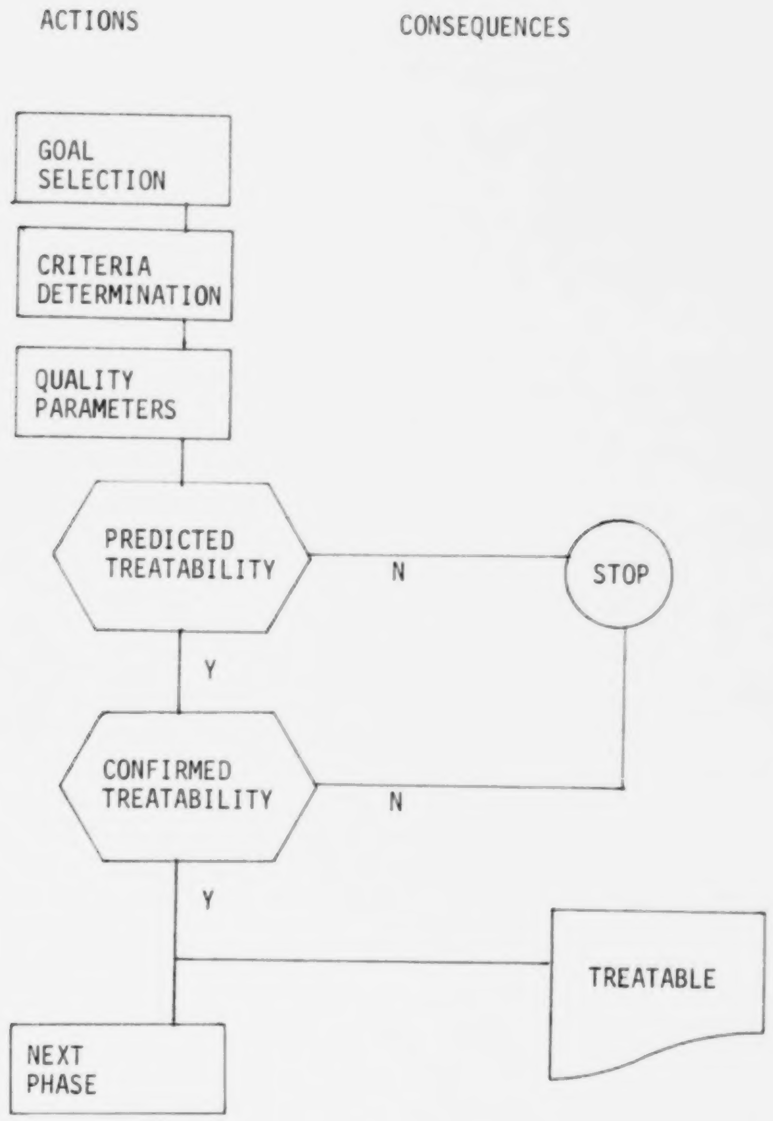
ACTIONS
CONSEQUENCES
GOAL SELECTION
CRITERIA DETERMINATION
QUALITY PARAMETERS
PREDICTED TREATABILITY
N
STOP
Y
CONFIRMED TREATABILITY
N
Y
TREATABLE
NEXT PHASE

Figure 166. Treatability Approach Flowchart

protocol should be completed. If reaction rate limits the process, this phase phase is omitted. At the same time, the ozone residual in the water will be predicted. This will be zero for the mass transfer limited case, some small but finite value in the quasi-mass transfer case, and determined by Henry's law in the reaction rate case.

In the mass transfer stage (Stage VI), the mass transfer model (Appendix D) is employed to optimize mass transfer and thus enhance and control the reaction. The volume of liquid to be treated will be known from a prior phase. Presumably the geometry of the contactor will be also fixed at this time. Results indicate that a narrow column diameter is more conducive to effective mass transfer than a wide one (although experiments show that reproducibility of results suffers with diameters less than 2 cm). As a first approximation, it may be assumed that gas holdup is relatively constant and any reasonable value may be used. The model is first run at different flow rates to determine the optimum gas flow. This may be then used to calculate the air:water ratio which is fed back into the ozone utilized stage. After this, the system is run under these conditions, the volume of air + water measured and the mass transfer coefficients calculated. Process configurations which may require an extension of the model may also be tested at this time.

In using ozone as a pretreatment for the GAC process, it is considered necessary that the ozone does not come into contact with the activated carbon itself. The reasons for this are two-fold. First, it is thought that the ozone will react with the carbon causing physical attrition and consequent head loss due to buildup of carbon fines. Second, the reaction of ozone with the carbon surface could act to alter the capacity or adsorptive characteristics of the carbon (9). In order to prevent ozone from contacting the carbon, use is made of a post contactor detention basin and measurements on ozone decomposition rates. In this stage (VII) of the protocol, ozone decomposition kinetic experiments are utilized to design the detention basin and to calculate the total ozone-organic contact time.

The last stage of the protocol involves ascertaining the effects of ozone on organic, inorganic, and biological water quality parameters under the conditions arrived at. Experience dictates examination of at least the following:

turbidity
pH
iron/manganese
alkalinity
dissolved oxygen
nitrogen speciation (high pH)
standard plate count/coliforms
presence of stable residual oxidants

The effects on organics may be ascertained by examining both substrates and products:

non-specific parameters (TOC, THMFP,UV)
group parameters (carbonyls, phenolics)

broad spectrum chromatographic profiling analysis
individual compounds of special interest.

Due to the focus of this investigation on micropollutant removal, a separate micropollutant subroutine for the protocol has been devised. A schematic is presented in Figure 167. Micropollutants may be examined individually or as a group. Once the micropollutant has been selected based on other considerations, the next step is to evaluate removal by simple stripping as opposed to ozonation. If stripping proves effective, the subroutine stops. If stripping proves ineffective, then ozonation is investigated. To characterize the ozonation of micropollutants, it is necessary to determine the physical-chemical mechanism of the process. This would include a determination of rate limiting step and stoichiometry. Appendix E presents a complete example of the protocol for the ozonation of the micropollutant diethyl phthalate.

The effect of the aquatic matrix should be assessed when considering ozonation of micropollutants. This matrix may exert an ozone demand that will compete with the ozone demand exerted by the pollutant under consideration. In addition to examining the total matrix, important inorganic and organic components can be examined individually. Identifying specific factors which affect ozonation can allow these factors to be manipulated or eliminated to gain control over the removal of micropollutants by ozonation.

The completed version of the protocol is shown in Figure 168. In summary two important points may be made. The first is that not all waters are ammenable to ozone treatment as a component of an ozone/GAC process. This is demonstrated by an initial treatability index and carries through the design process into the effects of ozonation. The second is that many concepts derived as part of this investigation may be applied directly to design and study of ozonation systems. These include:

- goal, criteria, parameter relationship
- ozone/GAC treatability index
- monitoring of substrate rather than oxidant
- application of ozone at point of highest demand
- breakpoint ozonation to determine contact time
- ozone utilized as a control parameter
- differentiation of mechanisms by rate determining steps
- use of models and mass transfer concepts
- ozone decomposition and post contactor detention basin
- separation of the stripping from the oxidizing function

Ozonation of Delaware River Water

With respect to organic non-specific parameters, ozone uniformly removed DOC and UV absorbance from the water. The degree of removal of DOC was ozone dose and contact time dependent; the removal of UV absorbance (A254) was more dependent on contact time and less on dose as confirmed in the O_3/SAND studies at the Pilot Plant (Tables 57 to 61). The organic group parameters measuring phenolic compounds were also reduced in Delaware River water by ozonation. The group parameters measuring carbonyl compounds increased as a

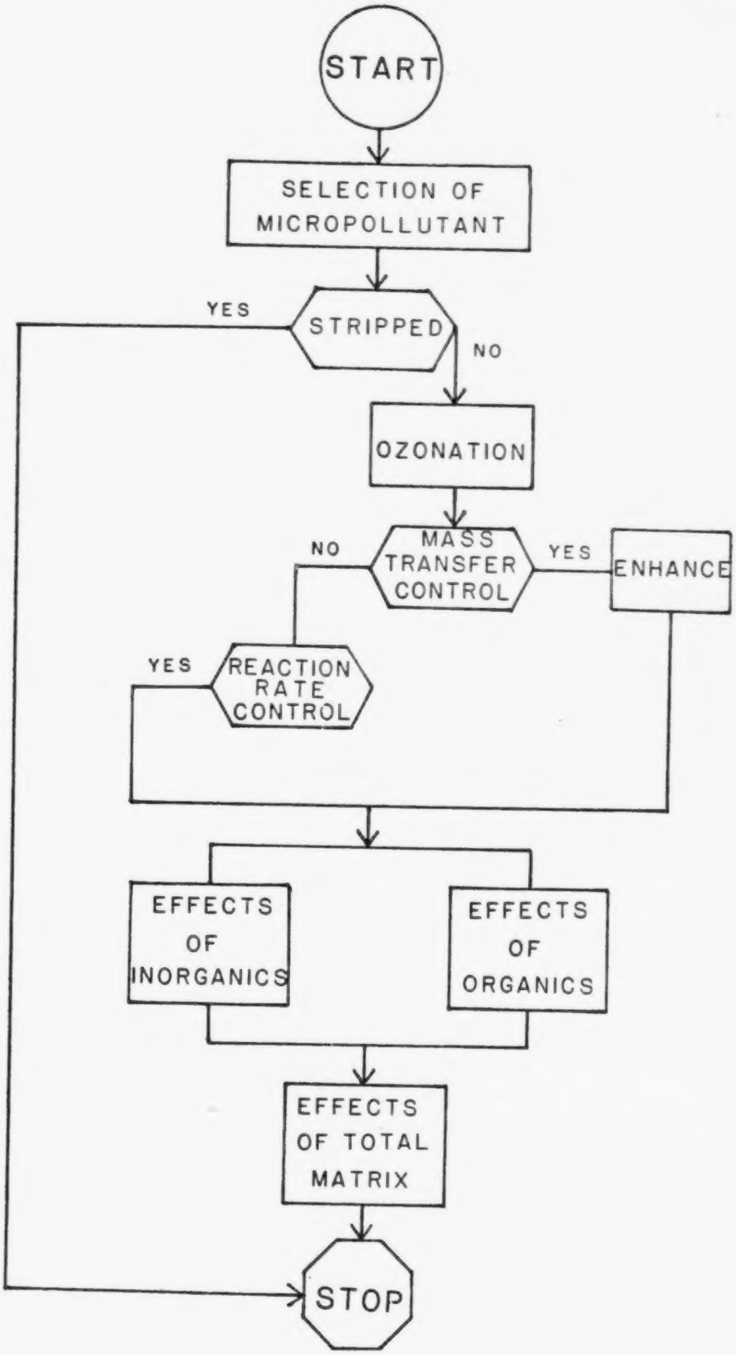
START
SELECTION OF MICROPOLLUTANT
STRIPPED
YES
NO
OZONATION
MASS TRANSFER CONTROL
NO
YES
ENHANCE
REACTION RATE CONTROL
YES
EFFECTS OF INORGANICS
EFFECTS OF ORGANICS
EFFECTS OF TOTAL MATRIX
STOP

Figure 167. Micropollutant removal flowchart.

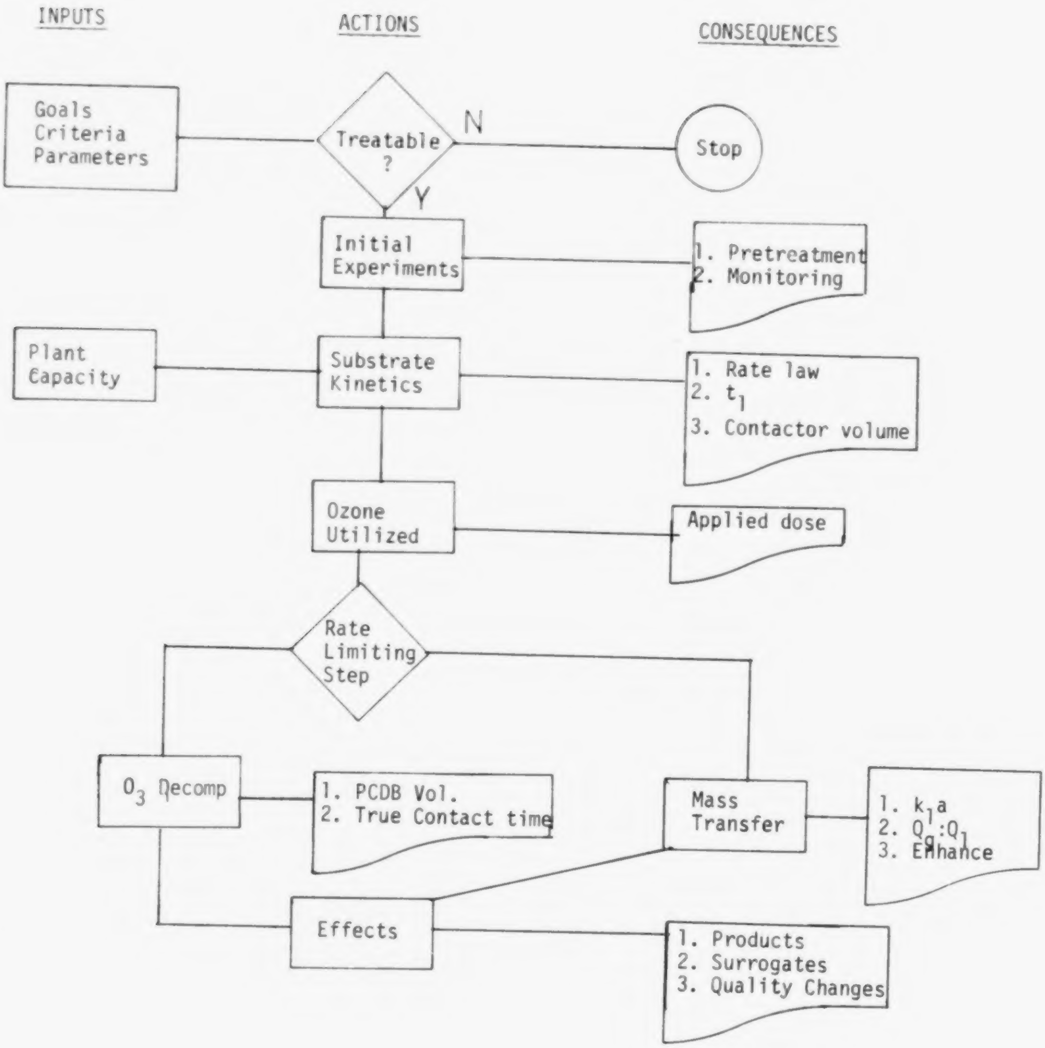
INPUTS
ACTIONS
CONSEQUENCES
Goals
Criteria
Parameters
Treatable ?
N
Stop
Y
Initial Experiments
1. Pretreatment
2. Monitoring
Plant Capacity
Substrate Kinetics
1. Rate law
2. t_1
3. Contactor volume
Ozone Utilized
Applied dose
Rate Limiting Step
O_3 Decomp
1. PCDB Vol.
2. True Contact time
Mass Transfer
1. k_la
2. $Q_g:Q_l$
3. Enhance
Effects
1. Products
2. Surrogates
3. Quality Changes

Figure 168. Complete protocol for ozonation.

results of ozonation. The effect of ozonation on THMFP was ambiguous, with increases, decreases, and no change in this parameter being noted as was subsequently noted in the studies at the Torresdale Plant and the Pilot Plant (Table 45).

The effect of ozone on inorganic water quality parameters was minimal. Ozone was shown to have an effect on pH, alkalinity, dissolved oxygen, and dissolved iron. The effect of ozone on pH was variable and not large. The effect of ozone on alkalinity increased as the alkalinity of the water increased. The net effect was no change in total alkalinity but a shift from bicarbonate to carbonate alkalinity with concommittant increase in pH. The effect of ozone on iron was to oxidize ferrous to ferric iron resulting in a precipitation of iron oxides.

Ozone was shown to be a good disinfectant in respect to aquatic bacteria for both Delaware and Schuylkill River systems. This effect was noted even at small doses and short contact times (see Table 26).

It was determined that ozone would have the greatest effect on humics in water treatment if applied prior to any other treatment. Once the material has been chlorinated, it becomes more refractory to ozonation. The higher the degree of pre-treatment, the more difficult ozonation becomes. If the target substrate is a micropollutant in the water as epitomized by diethylphthalate, this conclusion is reversed, i.e. the higher the degree of pre-treatment, the more readily removed is the micropollutant.

Ozonation of High Molecular Weight Materials (humics)--

The reaction of ozone with humic materials is generally limited by the mass transfer of ozone into the water, i.e. in a series of physical and chemical reactions with humics, the mass transfer step is slower than the ozone decomposition step or the chemical reaction with humics step. The rate of degradation of humics by ozone is a function of ozone dose or concentration in the water, substrate concentrations, and pH. Often these dependencies are complex and may not be represented by a simple function. In general, at steady state for a mass transfer limited reaction:

$$\text{Mass transfer} = \text{reaction rate}$$
$$k_L a(C_s) = k(S)^n(OH^-)^m D^p$$

where n, m and p are the exponents in the rate law (e.g., for humus, n & p = 1 and m = 0), S is th substrate concentration, D is the applied ozone dose, C is the saturation ozone concentration and $k_L a$ is the mass transfer coefficient. Many of the reactions studied may also be represented by the pseudo first order rate law:

$$\frac{dS}{dT} = k(S)$$

if the other factors are held constant. The mass transfer component is related to bubble size and gas flow. In these experiments, the superficial gas velocity was found to be the most important physical factor that controls ozonation. If extrapolated to continuous systems this parameter must be replaced by liquid velocity.

It was found that, since numerous factor affect the ozonation process these should be controlled or specified in order to ensure reproducibility of results and to enable comparisons between laboratories. It is thought that control of these variables will eliminate some of the controversies and ambiguity surrounding such subjects as the ozonation of phenol or trihalomethane precursors. The factors identified are:

1. Solution/matrix effects
   a. pH
   b. ionic strength
   c. buffer composition
2. Ozone concentration effects
   a. ozone dose
   b. ozone utilized
3. Process rate effects
   a. rate limiting step
   b. mass transfer coefficient in the contactor
   c. superficial gas velocity
   d. analysis of inhibitors/scavengers (oxidation competition value)
   e. contact time
   f. sample volume in a batch system; flow rate in a continuous system.
4. Method of monitoring the reaction
5. Ozone generator feed gas composition

In the ozonation of humics, certain factors concerning the substrate also need to be defined. Those which have proven useful for delineation of high molecular weight materials in this investigation are:

--dissolved organic carbon
--A420 (Apparant color)
--A254 (Apparent aromaticity)
--phenolic content
--trihalomethane formation potential
--fulvic-tannic-lignosulfonic analysis
--% molecular size greater than 1000 Daltons (ultrafiltration)

In general, reaction of ozone with humics reduces the non-specific parameters of DOC, A254, A420 and size. Phenolics are also decreased. If the system is unbuffered, the pH is lowered. This is probably related to production of carboxylic acids. Carbonyl compounds, especially low molecular weight aldehydes are increased. There is some evidence for mineralization of carbon in addition to conversion to lower molecular weight organics as shown in the pilot scale ozonation studies (see Discussion Section).

Oxygen was found to both react with some of the substrates and also strip volatiles out of solution. In general, oxygen caused oxidative coupling at high pH with a slower rate than ozone. No oxidative degradation by oxygen was observed. Mass balances indicate that a substantial amount of low molecular weight volatile materials formed by ozonation of humics may be stripped out of solution thus adding to ozone's capability for organic removal.

The mass transfer efficiency was evaluated for several contactors used in the study. In addition, a mathematical model of mass transfer was constructed (Appendix D) and validated by numerical comparison of predicted values to experimental values. Other points of validation included comparisons based on contactor diameter, gas flow rate, and catalysis/inhibition. Carbonate and hydrogen peroxide were found to inhibit the reaction between ozone and humic acid whereas ferric chloride, chlorine, and a natural water matrix had no effect.

Ozone Utilized

Ozone utilized was found to be a useful parameter to be examined in ozone treatment processes. This parameter can be used for determining reaction rates and stoichiometries for reactions of specific compounds with ozone or for comparisons among waters of different ozone demand.

A direct relationship was found between ozone utilized and organic loading. This measurement was found to be unaffected by the presence of ionic materials or pH. Chlorine was found to show a strong interference. The measurement was used to understand the Pilot Plant ozonation systems.

Ozone Kinetics

Generally, micropollutants fall into three categories: stripped, ozone mass transfer or quasi-mass transfer rate controlled, or chemical reaction rate controlled (See Figure 35). Based on these mechanisms, control over the ozonation process may be established. Compounds which are readily removed by stripping should not be removed by ozonation. A mass transfer or quasi-mass transfer rate may be enhanced by increasing the ozone applied dose or the k_La. To enhance a reaction rate limited mechanism, it would be necessary to add a catalyst or alter the aquatic matrix by some means such as raising pH.

The effect of pH should be considered in any ozonation reaction. pH is primarily important because the speciation of ozone changes as a function of pH. In addition, the micropollutant itself may undergo a chemical change due to alterations in the pH. The mechanism of the reaction may also change with pH.

The real water matrix is important in determining the overall rate of ozonation of a micropollutant. Various organic, inorganic, and physical factors may interfere with the ozonation process. A few of these factors may enhance the rate, but generally, compounds in addition to the micropollutant of interest appear to exert an inhibitory effect.

In terms of the removal of diethylphthalate, ozone is a very effective treatment. Several important conculsions concerning this process are:

- --the ozonation of diethylphthalate is fast and mass transfer controlled at pH 8; at pH 3, the reaction is slow and reaction rate limited.

- --pH significantly affects the rate of ozonation. The rate of ozonation of diethylphthalate varies to the 0.142 power of OH^- (measured in mM). This relationship was found to hold up to pH 8. Above this, the reaction did not proceed faster probably due to the mass transfer rate limitation.

- --as expected for a mass transfer limited reaction, increasing the ozone dose increased the reaction rate at pH 8. The rate was found to vary to the 0.848 power of the dose.

- --ionic strength appears to affect the ozonation process only to the extent that it controls the buffer capacity. Low ionic strength solutions do not provide enough buffer capacity so that the pH decreases upon ozonation causing a net decrease in the ozonation rate.

- --carbonate drastically inhibited the reaction of ozone with diethylphthalate. Iron and kaolinite had small enhancement and inhibitory effects respectively. Ozonating the substrate in the Delaware River matrix caused a 30% reduction in the rate of ozonation which could not be accounted for by pH or ozone dose effects.

- --the optimal point of application of ozone as a unit process for micropollutant removal at Torresdale is prior to rapid sand filtration (CLAR (TP)) and post chlorination. This contrasts with the optimal point of application for humics removal. Pre-ozonation as practiced in the pilot plant improved the rate of ozonation compared to raw water or treatment plant water.

- --aldehydes and ketones were found and quantified for the reaction of ozone and diethylphthalate. Hydroxylation of the ring was found to be a minor component of the degradation of DEP by ozone and oxidative coupling was not observed.

Appendix D should be consulted for a detailed evaluation of the diethyl phthalate ozone reaction.

PILOT-SCALE STUDIES

The objective of the pilot scale studies was to determine the efficacy of the unit operations of ozonation and GAC treatment for removing DOC and trace organic substances of health concern at the ng/l to ug/l level. The unit operations of GAC and ozone were examined alone and in combination, and in both the presence and absence of chlorine. Since the effectiveness of these treatments are dependent upon the type and degree of pretreatment received, the following discussion will first focus upon the efficacy of the conventional treatment systems. Within this framework, a clear understanding of how TOC removal can be enhanced prior to treatment with GAC will be described. Following this will be a discussion of the ozonation process. Lastly, the discussion will focus on the relative effectiveness of the various GAC systems.

Conventional Treatment

It was demonstrated in the results section that more effective reductions in dissolved organic carbon (DOC) and trihalomethane precursor (THMFP) levels were evident through the Pilot Plant conventional treatment processes than through the Torresdale Plant processes. Two factors appear to be of primary influence: (1) a more efficient removal of the organics in the upflow sludge-contact clarifier of the Pilot Plant than in the crossflow flocculation/sedimentation basins of the Torresdale Plant, and (2) the absence of any residual disinfectant through the Pilot Plant. This second factor is of significance only if the microbial population in the Pilot Plant unit processes were able to utilize a portion of the DOC as substrate.

Pilot Plant results of the ozone/sand system (to be discussed later in this section) verify that the bacterial removal of biodegradable DOC is essentially complete in a sand bed of EBCT=15 minutes. Therefore, in order to determine whether any of the organics in the non-disinfected, settled river water were biodegradable, Pilot Plant raw water basin effluent (Site 11) was applied directly to a sand bed (EBCT of 30 minutes) and DOC levels through the bed were measured. Figures 169 and 170 show the DOC levels through the sand bed in terms of instantaneous concentration and cumulative distribution function, respectively. Over the operating period of the system (3/9/81 to 8/14/81), a statistically significant average reduction of 261 ppb DOC was observed (t-test with $\alpha = 0.05$). Since the sand bed was incapable of any organic adsorption, the observed organic removal is attributed to biological degradation. Operational problems with this sand system (i.e. low and no flow conditions) did, however, result in upsets to the bed's bacterial community. Figure 171 confirms that although the bacterial levels through this sand system averaged 10^6 to 10^7, there were rapid fluctuations in this population. Because of these upsets, the average DOC reduction of 261 ppb is considered a conservative estimate of the biodegradability of the organics present in the Delaware River during this time period.

A similar utilization of sand columns showed that while half of these biodegradable organics passed through the clarifier (Site 13), none of the DOC in the rapid sand filter effluent (Site 14) was easily attacked by bacteria. These results indicate that the readily biodegradable organics in the

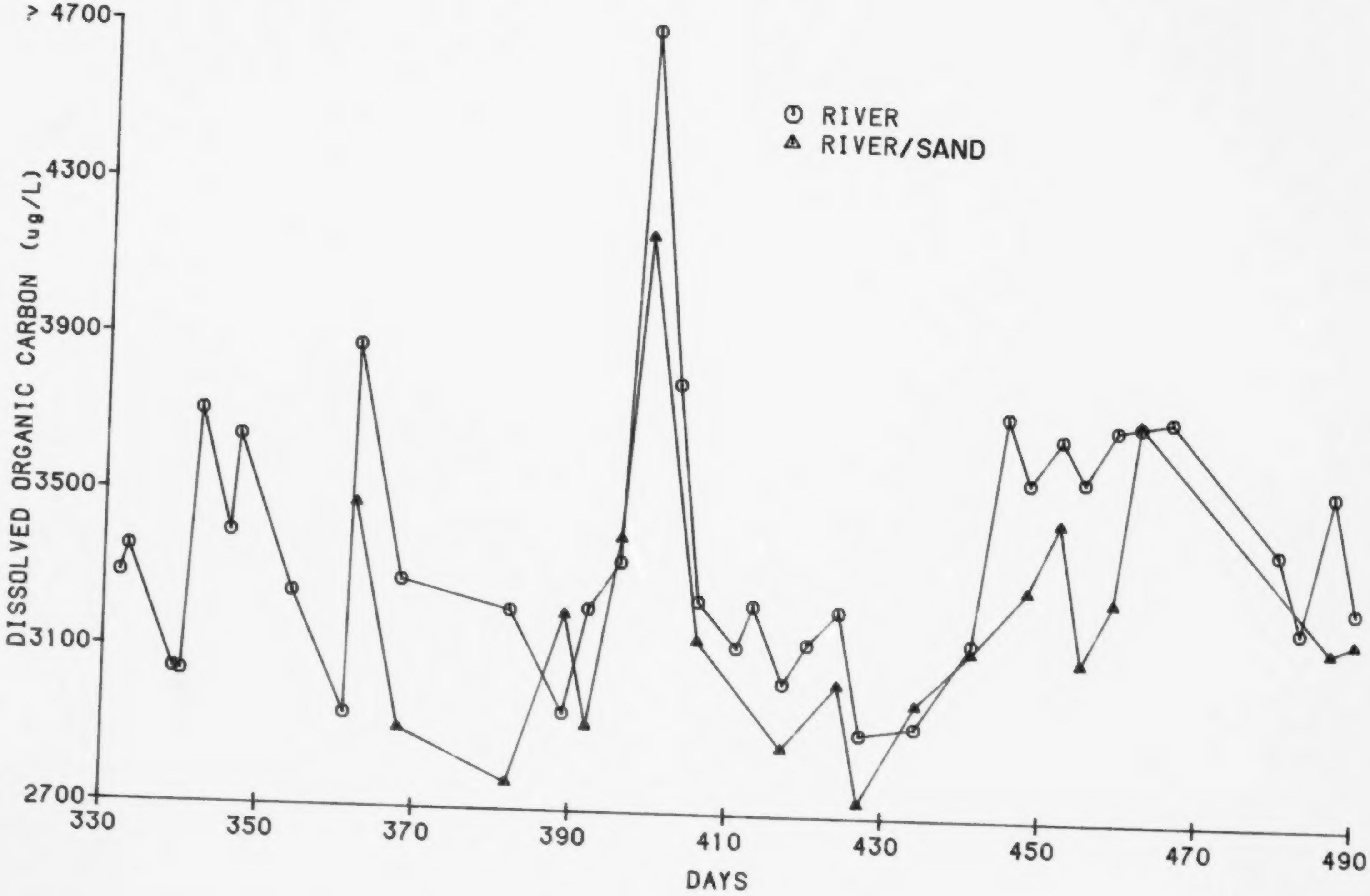

Figure 169. The effectiveness of sand filtration in reducing DOC levels in Delaware River water.

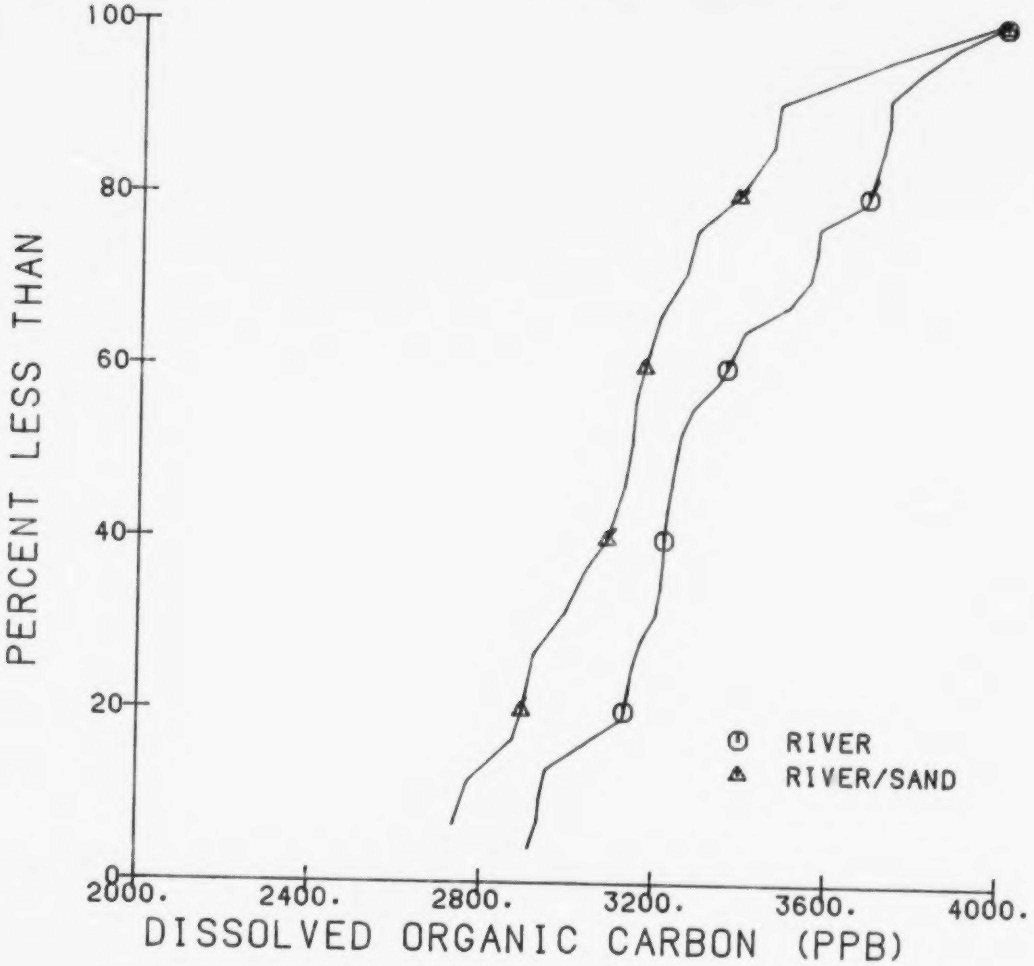

Figure 170. DOC levels through a sand bed applied with Delaware River water.

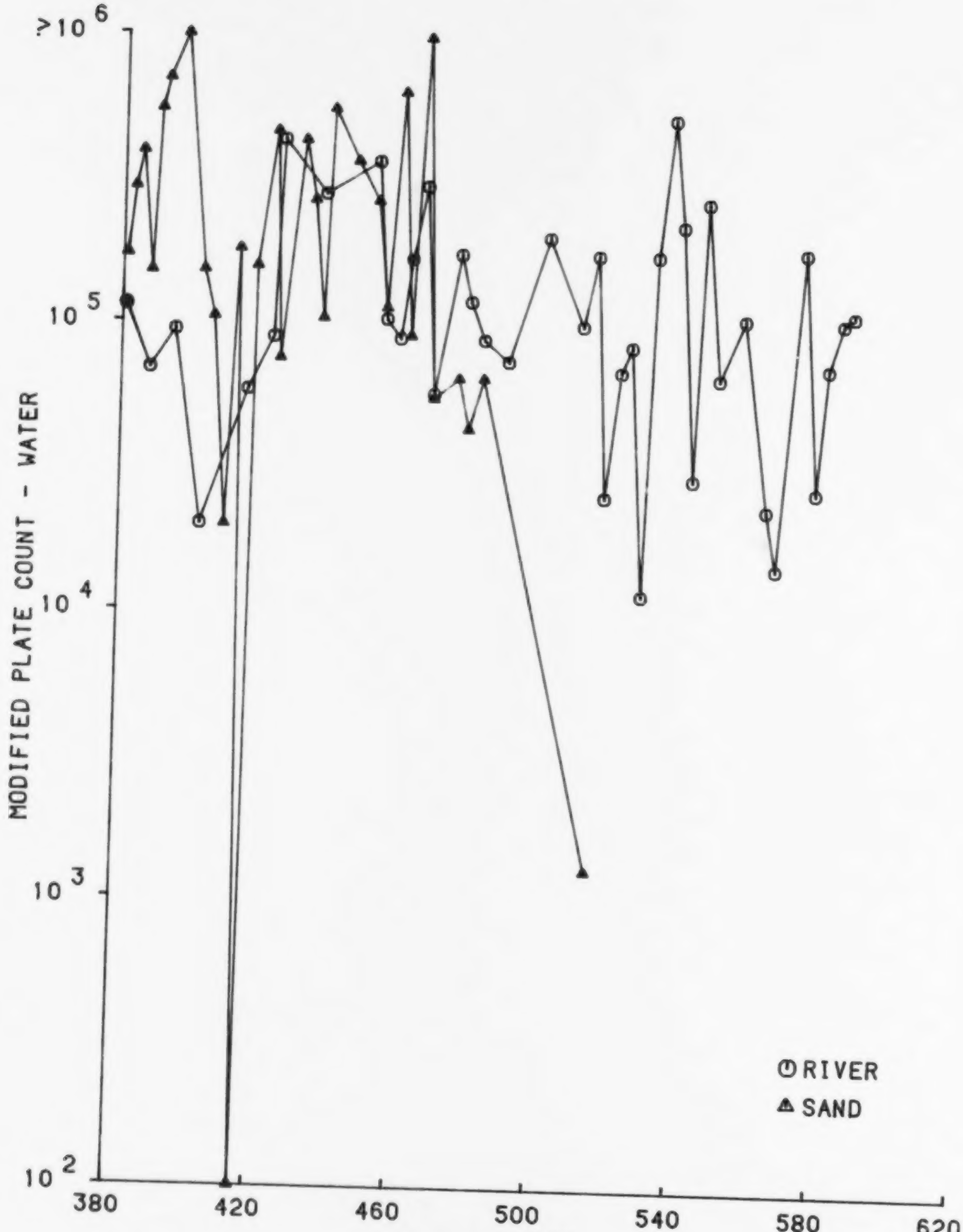

Figure 171. Heterotrophic bacterial levels through a sand bed applied with Delaware River water.

influent river water are effectively removed in a conventional treatment train that does not include disinfection. This conclusion verifies similar work done by Feissenger et al (169) at the Morsangsur-Seine Waterworks who found that, in the absence of prechlorination, their conventional treatment pilot plant removed 250% more TOC than their comparable full-scale conventional treatment plant which had prechlorination (2.0 ppm chlorine dosage). As a comparison, the Philadelphia Pilot Plant removed 290% more DOC than the full-scale Torresdale Plant.

Another possible cause for deviations in water quality in the effluent from the Torresdale and Pilot Plant conventional treatment systems may be due to the different water intake frequencies of the two plants. The Torresdale Plant takes advantage of the tidal fluctuations of the Delaware River Estuary by raising its intake gates at high tide and closing them near low tide. The Pilot Plant, however, continuously draws its water from the Delaware. By examining the time distribution data for 1,2-dichloropropane (DCP) at the rapid sand filter effluents of the Torresdale and Pilot Plants (Figure 41), some conclusions may be drawn as to the relative quality of the two influents. This figure shows that both systems responded similarly to changes in DCP concentration. However, the Pilot Plant rapid sand filter effluent consistently had lower DCP levels (average DCP of 4.3 ppb) than the Torresdale Plant (average DCP of 5.5 ppb). This may also be seen in Figure 172, which shows the cumulative distribution function for DCP. A t-test performed on the data (α =0.5) showed a statistically significant difference between the DCP levels at the two sites. Thus, a difference was observed in DCP concentrations in the different tidal cycles of the Delaware River Estuary.

GC-FID profiles from the purge and trap analysis of the rapid sand filter effluents of the two plants showed between 19 and 31 GC peaks (e.g. (Figures 58 and 59). Of these, twenty-two GC peaks were routinely quantified (Tables 15 and 16). The compounds which were probably included in the purge and trap analysis but not quantified were the chloromethyl-butenes and butanes, tetrahydrofurans, as well as other compounds identified by GC/MS below the boiling point of dichlorobenzene (Table 43).

Table 42 presented the average concentrations of the volatile organics which were identified by the purge and trap method in the Torresdale and Pilot Plant rapid sand filter effluents. In general, the compounds were present in slightly lower concentrations through the Pilot Plant. This is again best explained by the tidal cycle effects as described for 1,2-DCP. Notable exceptions to this were the trihalomethanes which were produced during chlorination and carbon tetrachloride which was introduced as a contaminant of the chlorine. The greatly reduced concentration of acetone through the Pilot Plant may have been due to its biodegradation through this nondisinfected conventional treatment system.

GC-FID profiles from the analysis of the MRR accumulators showed that an average of 233 GC peaks of >0.2 ng/l were present in the Torresdale Plant RSF effluent. This compares with an average of 167 GC peaks found in the Pilot Plant RSF effluent. This difference is accounted for by two factors. The first factor is that the different intake systems of the two plants may have caused higher organic loads at Torresdale. The second

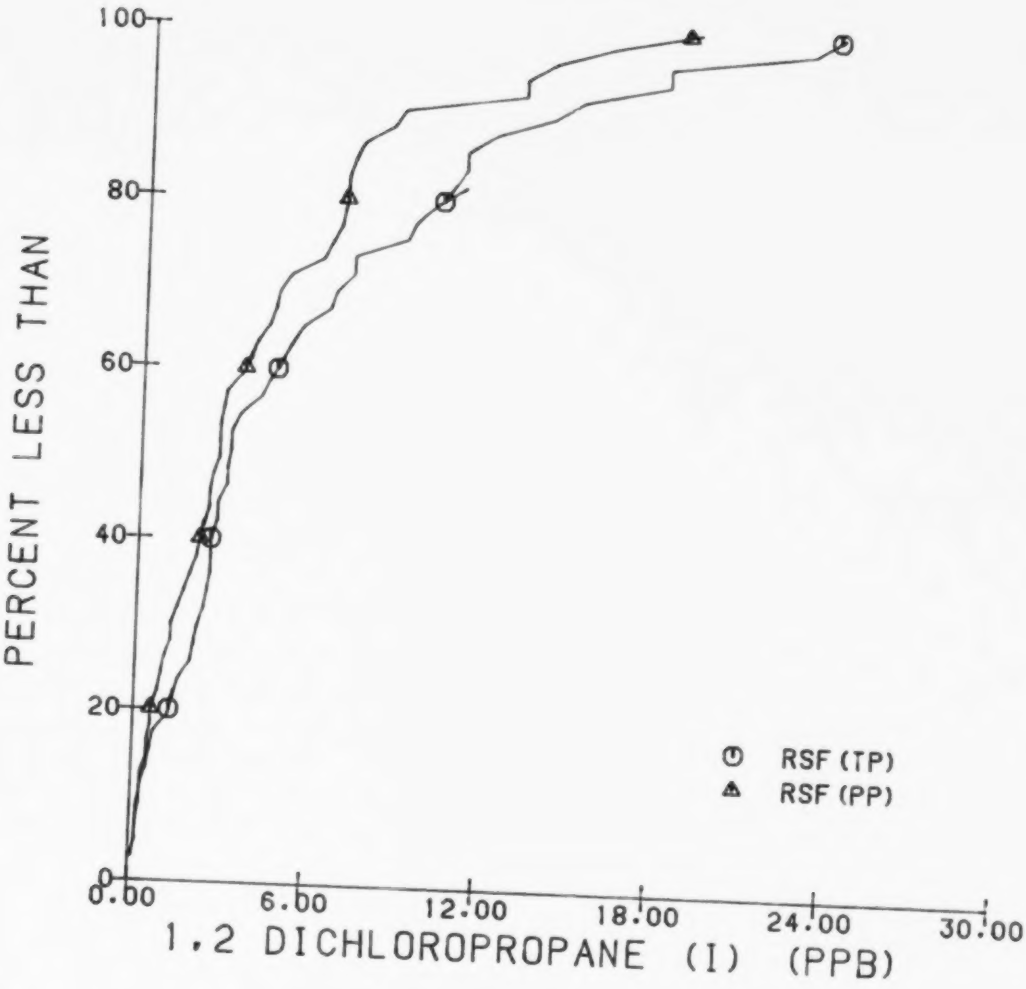

Figure 172. 1,2-Dichloropropane levels in the Torresdale and Pilot Plant RSF effluents.

factor is the effect of prechlorination. Prechlorination at Torresdale results in the production of many new nonpolar compounds that could be analyzed by GC. These compounds could arise from oxidation and/or substitution of low MW organics and high MW humics by chlorine. As expected, more chlorinated compounds were identified in the Torresdale plant rapid sand filter effluent than in the Pilot Plant. These include 1,1,1-trichloroacetone and chlorinated butanes and butenes as well as the trihalomethanes. Trichloroacetone has also been shown previously to be a product of the chlorination process at Torresdale (170). Greater biological degradation through the Pilot Plant also alters the mixture of organics present in the effluent. These products will not be chlorinated but are expected to be oxygenated and more highly polar. These polar compounds may not be isolated and measured by th MRR method.

Figure 63 shows that there were twice as many peaks in the Kovats Index range of 800 to 1400 in the Torresdale Plant effluent than in the Pilot Plant effluent. 33% of the compounds in the Torresdale Plant effluent had concentrations greater than 2.0 ng/l. This compares with 16% of the peaks present at the Pilot Plant (Table 44). Therefore, the Torresdale Plant had twice the number of organics in the KI range of 800-1400 and four times the number of organics with concentrations greater than 2 ng/l. It must be restated that the MRR method includes a base extraction cleanup step that is necessary for capillary column gas chromatography. This step could remove oxygenated acidic compounds which are produced by biological or chemical oxidation.

In conclusion, a different mixture of organic compounds were present in the effluents from the two conventional treatment plants. This conclusion was based upon measurements of TOC, THMFP, and volatile (halogenated and nonhalogenated) and semi-volatile organics. There were more compounds present, in higher concentrations, in the chlorinated Torresdale Plant than in the Pilot Plant. In addition, there were more chlorinated compounds.

Ozonation System

The efficacy of the Torresdale and Pilot Plant ozonation processes for removing DOC, A254 and THMFP was demonstrated in Figures 42 to 45. A summary of the average removals was presented in Table 45. The Torresdale and Pilot Plant ozonation systems reduced DOC levels on the average 107 ppb and 204 ppb, respectively. Only a small percentage (<1%) of these reductions may be accounted for by the volatilization of chloroform and other easily stripped organics, as determined by performing mass balances across the contactors. The remainder and major portion of the DOC reductions were apparently due to either the complete oxidation (i.e. mineralization) of organics to carbon dioxide or, alternatively, to the formation of volatile compounds (such as acetone) which were then effectively stripped from the process stream.

Less DOC removal was observed through the Torresdale ozonation system than through the Pilot Plant system. This is of particular interest since there was a 140% greater organic loading onto the Torresdale ozone contactor. One explanation for this is that the chlorination process produced compounds that were more resistant to further oxidation by ozone. However, an alternate explanation for at least a portion of the better performance may be that biological degradation of DOC occurred in the Pilot Plant retention tank. Although the Pilot Plant contactor achieved a 99.8% bacterial kill, the ozone- and chlorine-free effluent of the Pilot Plant retention tank exhibited a 40-fold increase in bacterial levels and a 40 ppb decrease in DOC. Whether this DOC drop was due to biological degradation or continuing chemical oxidation could not be determined. However, no similar DOC reductions were observed through the Torresdale retention tank.

The Pilot Plant ozonation system was also more effective than the Torresdale system in reducing A254 and THMFP levels. A254, which was reduced by nearly 50% through the Pilot Plant ozone contactor, was reduced by only one-fourth through the Torresdale system, indicating a greater reduction in aromatic compounds and other compounds with double bonds when nonchlorinated water is ozonated. Caution must be exercised when interpreting A254 results, however, since this parameter is a function of not only the concentration, but also the type of chemical species present in the water sample. THMFP levels, which were reduced somewhat through the Pilot Plant ozonation system, actually increased slightly through the Torresdale contactor. Here again, any correlation observed between the degree of ozonation and the THMFP levels was found to be at best, ambiguous (see Results Section: Ozonation Studies).

Because of the problems associated with the interpretation of the A254 and THMFP data and the limited information derived from the DOC results, another parameter was needed for measuring the effectiveness of the ozonation process in producing biodegradable organics from the highly complex, biorefractory compounds. This was accomplished by applying Pilot Plant ozonated water to a biologically active sand bed (O_3/SAND$_{30}$). This system is biologically active since the applied water is both free of any residual disinfectant and high in dissolved oxygen. Therefore, biological growth should be limited only by substrate availability. The discussion of the minicolumn results will demonstrate the viability of using these sand contactors as a measure of bioactivity and biological degradation of organics.

Figure 46 showed the DOC levels through the Pilot Plant ozone contactor and through the first 15-minute O_3/SAND system. Over the one year period shown, DOC was reduced an average 204 ppb through the ozone contactor and an additional 227 ppb through the O_3/SAND$_{15}$ bed. The second successive sand bed (the O_3/SAND$_{30}$ system) showed no appreciable increases in DOC reductions indicating that the 15 minute EBCT was ample time for all biodegradable organics to be removed from the process stream. As described previously, the influent water to the Pilot Plant ozone contactor was similarly tested and found not to contain any readily biodegradable organics. It was thus concluded that approximately one-fourth of the DOC entering the Pilot Plant ozone contactor was oxidized; either completely, to carbon dioxide, or partially, to readily biodegradable compounds.

A similar test could not be performed using the Torresdale ozone contactor effluent since the free chlorine residual would inhibit any bacterial growth on a sand bed. However, since there was evidence of complete oxidation of organics in the Torresdale ozone contactor, it is most probable that partial oxidation also occurred. And, given the fact that free chlorine is destroyed in the top few inches of a carbon bed (37), the Torresdale ozonation system also resulted in additional substrate for the bacteria on the GAC beds.

Ozone utilized was also found to be a useful parameter with which to measure the relative effectiveness of the ozonation systems. Figures 173 and 174 compare ozone utilized and Δ DOC through the Torresdale and Pilot Plant ozone contactors, respectively. The Torresdale Plant contactor had an average ozone utilized value of 1.2 mg/L for the year while the Pilot Plant averaged 1.6 mg/L (Table 5). Both ozone contactors exhibited lower ozone utilized values during days 180 to 360; Pilot Plant ozone utilized decreased from 2.0 mg/L to 1.0 mg/L while the Torresdale Plant ozone utilized decreased from 1.6 mg/L to 0.7 mg/L. This trend may be due to seasonal changes in which less oxidation occurs during the winter months. DOC removal through the ozone contactors, an indication of the degree of organic oxidation, also showed less DOC removal for days 180 to 360. For the Pilot Plant, the average DOC reductions decreased from 306 to 136 ug/L; for the Torresdale Plant, from 133 to 95 ug/L. These results follow the trend observed for the ozone utilized values and indicate that a relationship between the two parameters may exist. Further studies would be required in order to determine whether ozone utilized results may be used for predicting the effectiveness of the ozone contactor for DOC removal, as described in the section on the bench scale ozonation studies.

The Torresdale and Pilot Plant ozonation data shows that, for the volatile and semi-volatile organics isolated by the purge and trap and XAD resin procedures, there is: stripping of non-oxidizable volatiles (e.g. $CHCl_3$); oxidation and/or aeration of other volatile organics (see GC Profiles, Figures 58 and 59); simultaneous production and stripping of volatile organics (e.g. acetone); and production by oxidation of semivolatile compounds (see GC profiles, Figures 60 and 61).

Laboratory and pilot scale data confirm that stripping of the non-oxidizable, purgeable organics occurred during the ozonation process (see Table 39 and Figures 49 to 53). This is also indicated in Figure 175 which shows that organics of boiling points less than that of a C14 hydrocarbon are purgeable (171). Additionally, the effect of aeration on the trihalomethane levels in the Torresdale Plant water may be seen in Table 73. With chloroform levels reduced an average of 37% (47% during the summer months), it becomes quite clear that preozonation can have a significant effect on the concentration of volatile organics, especially at times of high volatile concentration. Figure 49 shows that the higher the levels of chloroform loading onto the ozone contactor, the more significant the role of aeration in reducing these levels.

It has been proposed that compounds having Henry's Law constants greater than 1×10^{-3} atm-m^3/mole are easily stripped form water (167). The Henry's Law constants for the specific volatile organics investigated in this study indicate that most should be stripped during the ozonation process. Table 74 shows the Henry's Law constants expressed as the ratio of the concentration in the air equilibrated with water at 20°C (172) and the percent removed by ozonation for several specific organic compounds. The increasing Henry's Law constants (K) represent increasing compound volatility. In general the

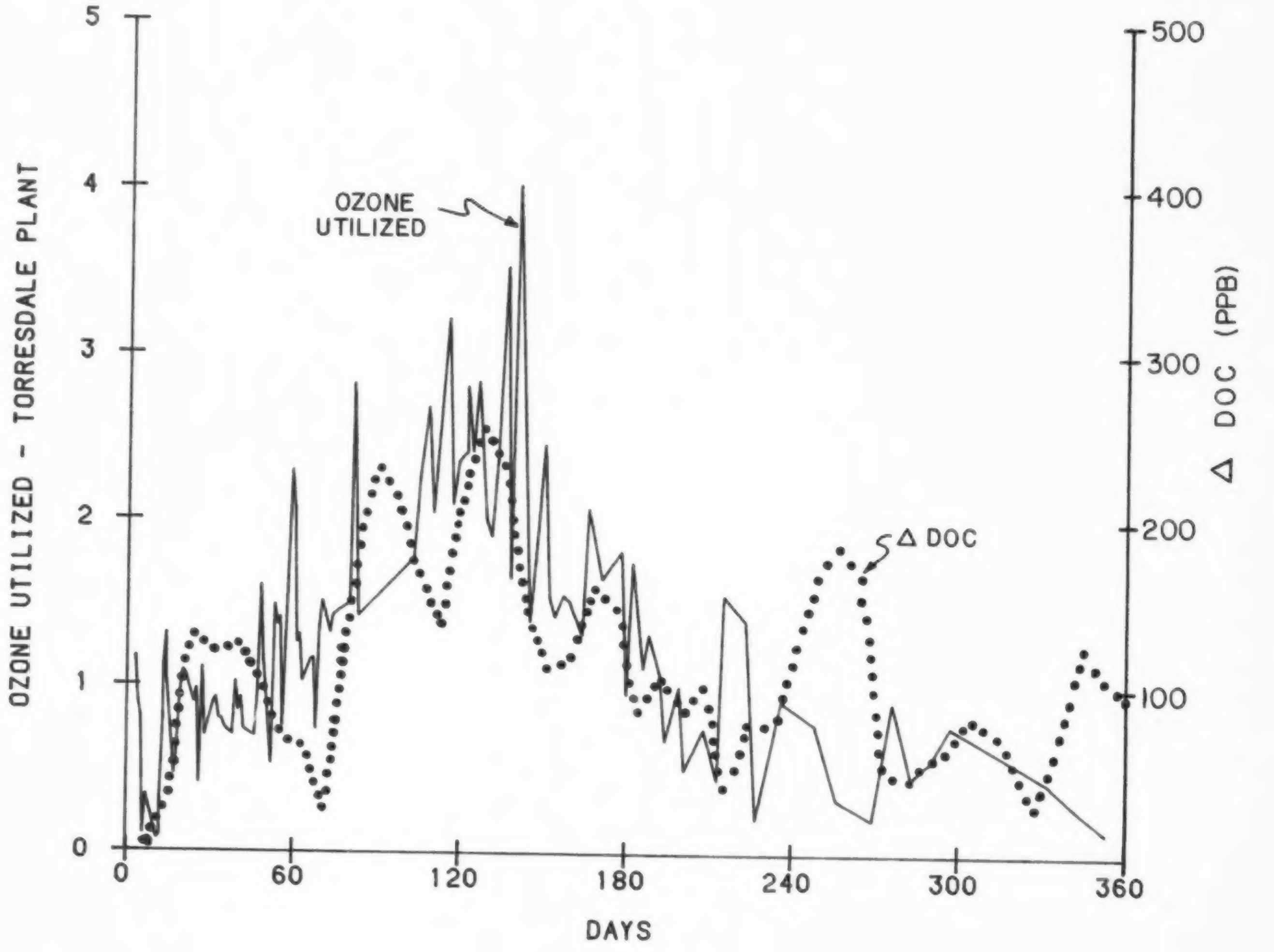

Figure 173. Comparison of Ozone Utilized vs. Δ DOC through the Torresdale Plant ozone contactor.

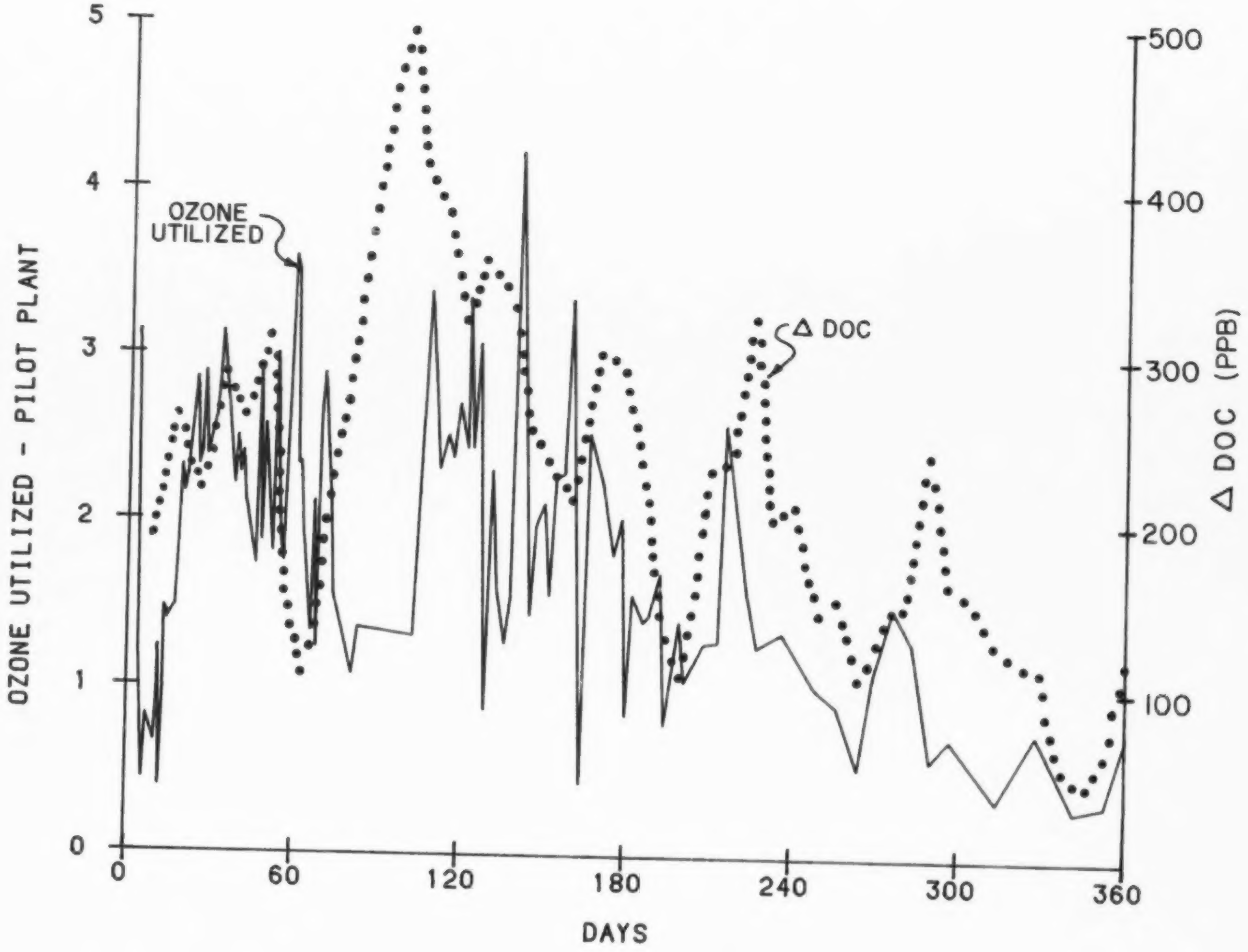

Figure 174. Comparison of Ozone Utilized vs. ΔDOC for the Pilot Plant ozone contactor.

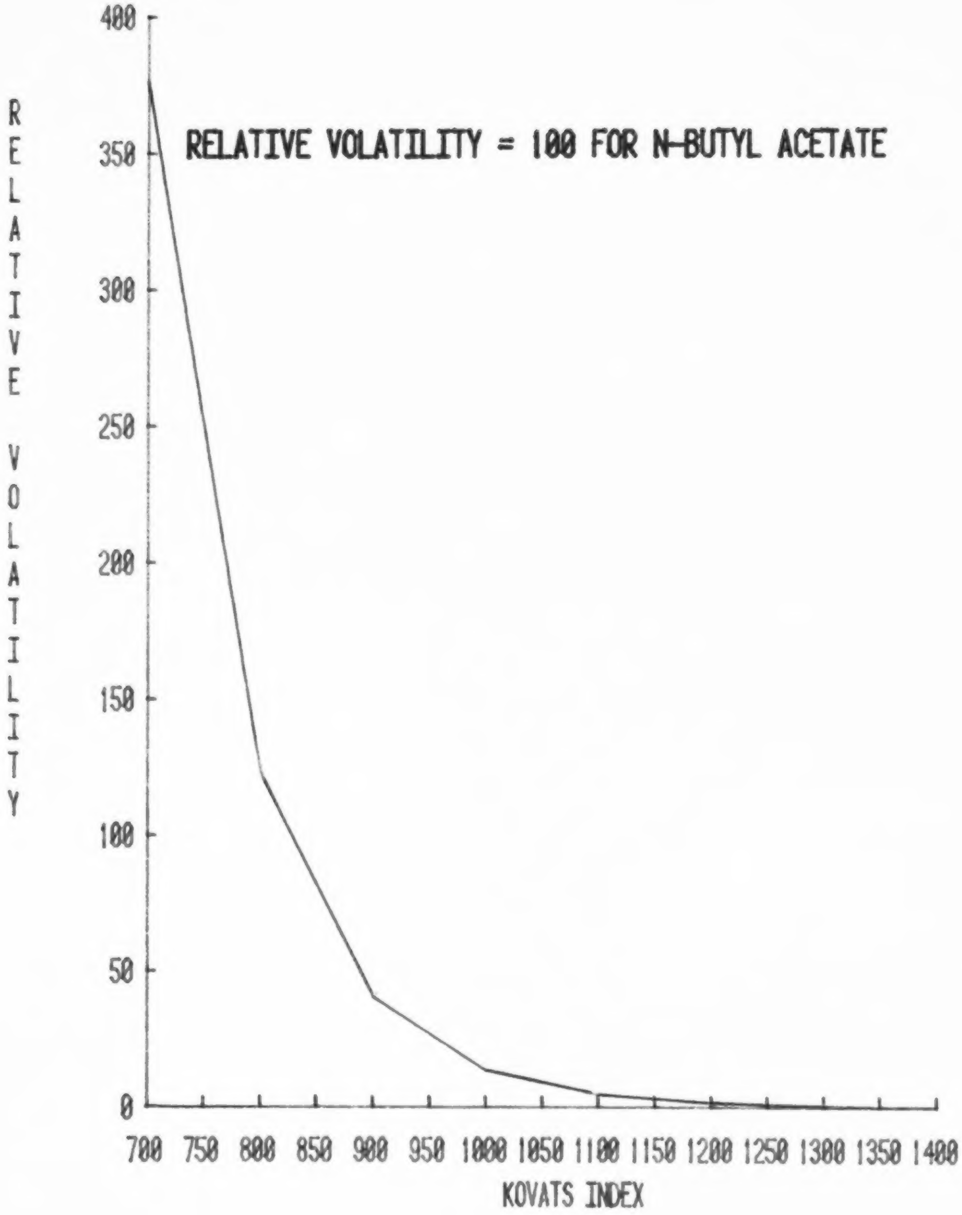

Figure 175. Aeration of organics below C14.

TABLE 73. AERATION OF TRIHALOMETHANES[1] THROUGH THE TORRESDALE PLANT OZONATION SYSTEM

	1-YEAR AVERAGES (4/80-4/81)			SUMMERTIME AVERAGES (7/80-7/81)		
COMPOUND	INF	EFF	%REMOVED	INF	EFF	%REMOVED
CHLO	73.	46.	37	123.	65.	47
DCBM	21.	15.	29	31.	19.	39
DBCM	5.6	4.8	14	7.5	5.8	23

[1] Based on weighted averages of weekly samples (ppb).

percent removals follow the increased volatility; only when influent concentrations were near the limit of detection (0.1 ppb) were large variations in this trend observed (e.g. benzene). It must also be stated that oxidation is also a factor in the percent removals especially for those compounds susceptible to oxidation by ozone (61, 63, 76). However, the extent of oxidation of a complicated mixture is unknown and is debated in the literature.

GC profiles comparing influents and effluents from the Torresdale Plant ozone contactor show 10% of the peaks decreasing by a factor of two or more while 5% increase during ozonation. This compares with 15% of the peaks decreasing and 5% increasing through the Pilot Plant ozone contactor (Table 48). These changes indicate aeration of volatile organics and production of oxidation byproducts. Since aeration of chloroform rarely changed its concentration by a factor of two or more, these estimates must be considered as conservative. Although only acetone and methyl ethyl ketone (tentative) have been identified by GC/MS as increasing (Table 49), other purgeable byproducts are indicated on the GC profiles (Figures 58 and 59).

Higher MW organics isolated by the MRR method specifically show 4 of 9 cases at Torresdale and 3 of 10 cases at the Pilot Plant where oxidation of the nonpolar organics is the primary mechanism of the removal of nonpolar organics during ozonation. The remaining cases show aeration of organics boiling below a C14 hydrocarbon to be the primary mechanism. Both processes are thus occurring simultaneously and dominance is a function of the variability of the mixture of the influent chemicals.

Ozone/Sand Studies --

The overall objective of the Ozone/Sand Studies was to optimize the Pilot Plant ozonation system for the oxidation of organic compounds. This objective was accomplished by altering the operating conditions of the ozone contactors and measuring corresponding changes in DOC mineralization and volatile stripping, as well as the partial oxidation of DOC to more readily

TABLE 74. COMPARISON BETWEEN HENRY'S LAW CONSTANTS AND THE OBSERVED REMOVALS OF SEVERAL COMPOUNDS DURING OZONATION

COMPOUND	K[a]	PILOT PLANT		TORRESDALE PLANT	
		CONC	% REM	CONC	% REM
1,2-Dichloropropane	122.92	4.5	33	6.1	21
Methylene Chloride	145.43	0.3	33	0.3	0
Chloroform	174.36	4.3	35	73	37
Benzene	242.50	0.2	0	0.2	0
Trichloroethylene	415.69	0.2	50	0.4	0
1,1,2,2-Tetrachloroethylene	678.30	0.4	75	0.4	75
Carbon Tetrachloride	1179.97	–[b]	–	1.0	80

[a] K = Henry's Law Constants at 20°C (172)

[b] average influent concentration below detectable limits (<0.1 ppb)

biodegradable forms. In order to determine organic biodegradability, DOC measurements were taken across sand beds which were operated in much the same mode as the O_3/Sand$_{15}$ system was during the pilot studies. Any and all DOC removal through these beds was considered due to bacterial degradation since no adsorptive mechanisms were at work. Certain checks were placed on our assumptions by adding similar sand beds both before and after the ozone/sand system and checking that none of the DOC entering the ozone contactor and none leaving the sand bed was in a readily biodegradable form.

The first ozone/sand study was initiated in order to determine whether the Torresdale and Pilot Plant ozonation systems would yield equivalent results when operated under identical conditions. Indeed, comparable removals of DOC, THMFP and A254 were achieved (Table 57). This confirmed that the differences noted in the effectiveness of the Torresdale and Pilot Plant ozonation systems during the pilot studies were attributable to the different quality of the two waters and not due to any inherent differences in the design or operation of the ozone contactors.

The following three studies were designed to determine whether an increase in ozone applied dose and/or contact time would result in an improvement in the effectiveness of the ozone/sand systems. The results indicated that additional reductions in DOC, THMFP, and A254 absorbance levels could be achieved through increases in the ozone/water contact time as observed in the bench scale studies (See Figure 26 and 29). Increases in the ozone applied dosage, however, proved to be of little added benefit. A synergistic effect was apparent when both parameters were increased simultaneously. The effectiveness of the Pilot Plant ozone contactors thus appears limited only by the available reaction time.

The final ozone/sand study investigated the effectiveness of the cocurrent versus the countercurrent ozone contactor designs. Under the conditions achieved in the pilot scale ozone contactors the direction of water flow had no significant effect upon the ability of the ozone system to oxidize organics. This confirms the findings of the other ozone/sand studies which showed that the only limit to further oxidation was contact time.

The ozone/sand system experiments also confirmed that the efficiency of aeration increased with increased contact time (Table 61) and that increased ozonation results in the increased production of oxidation byproducts. Acetone, for example, increased >25% during sampling periods with increased contact time and dose. Toluene (contact time) and benzene (contact time and dose) showed, on occasion, increases >25%. These aromatic compounds have been shown previously to increase in this fashion during ozonation of sewage (168).

Increased ozonation and contact time did not noticeably affect bacterial levels on the sand or in the system effluents. Bacterial levels in the effluents were comparable to or slightly higher than those in the sand and GAC effluents of the original pilot study. Although bacterial levels in the sand column effluents were comparable to those of the carbon effluents, bacterial populations on the sand were found to be lower than those on the carbon by an order of magnitude. This may indicate the greater availability of bacterial attachment sites on carbon than on sand.

In summary, the ozonation process reduced TOC by chemical oxidation to carbon dioxide as well as by enabling subsequent biodegradation as shown on the O_3/SAND columns. Although volatilation was found to be of little benefit in overall organic removal, it resulted in a considerable reduction in the concentration of the specific organic compounds of health concern, as determined by the purge and trap technique. However, evidence of the production of other organics of unknown identity and health concern were observed by GC profile analysis of volatile and semi-volatile organics. When chlorination preceeds ozonation, the production of chlorinated compounds which are apparently more resistant to further oxidation by ozone result. Therefore, oxidation of organics via ozonation appears less effective when prechlorination is employed.

Adsorption Systems

GAC can remove DOC and THMFP while removing ng/l to ug/l concentrations of trace organics of health concern. The primary concern for practical use of GAC is lowering its operating costs by increasing its useful life. Figure 1 showed the design elements utilized based up health effects prioritization (Table 1) for the removal of ug/l amounts of volatiles such as chloroform and other trace organics at the ng/l level in the presence of mg/l TOC.

The primary focus of the following discussion is to describe how the removal of high molecular weight organics (as measured by dissolved organic carbon, DOC) was enhanced through changes in the methods and degree of pretreatment. While the high molecular weight organic compounds found in the drinking water (which account for about 90% of the total organic carbon) are not of direct human health concern, some are precursors to potential carcinogens (e.g. chloroform) while others may compete with the more harmful organics for the limited adsorption sites available on the carbon. Following this discussion, the question of how this increased DOC removal affects the efficacy of the GAC system in removing the trace organics of health concern will be addressed.

Each of the four adsorption systems operated during the pilot scale testing encountered varying levels of applied organic loads. In general, the following trend developed:

$$GAC(TP) > O_3/GAC(TP) > GAC(PP) > O_3/GAC(PP)$$

where the GAC(TP) system experienced the highest organic loads and the O_3/GAC(PP) system experienced the lowest. This was observed for all of the organic parameters measured, including dissolved organic carbon and the volatile and semivolatile organics measured by the purge and trap and MRR accumulator methods, respectively. The Pilot Plant adsorption systems experienced lower applied organic loads compared to the Torresdale Plant systems, because of the reasons outlined in the previous section on the conventional treatment processes. Organic levels decreased through the ozonation systems due to the production of CO_2 and the subsequent biodegradation of the partially oxidized products and the volatilization of trace organics. In general, pretreatment appeared to have a greater influence on the concentration and types of organics applied to the GAC beds than did preozonation.

TOC Criteria for GAC Regeneration--

Table 75 presents the estimated bedlife of the various adsorption systems based on effluent DOC criteria ranging from 0.5 to 2.0 ppm. The symbol NR, signifying that no regeneration of the carbon would be required to maintain a given effluent criteria, is based upon consideration of the historic DOC levels in the water applied, and the behavior of the system under steady-state conditions. The table shows that preozonation of the applied water results in a significant improvement in the bedlife of the GAC bed when a DOC criteria of 1 ppm or less is applied. For criterion above 1 ppm, some of the GAC systems require no preozonation or carbon regeneration in order to maintain the effluent criteria.

Pretreatment processes also greatly affect GAC bedlife, as is exemplified by an examination of comparable adsorption systems of the Torresdale and Pilot Plants (Table 75). This importance is also demonstrated in Figure 176, which presents the average DOC levels in the effluents of the various treatment processes. Five locations are shown, beginning with the rapid sand filter effluents of the two plants and then continuing through the advanced water treatment systems. For all locations, the taller bar represents the Torresdale Plant; the shorter, the Pilot Plant. All values have been rounded to the nearest 25 ppb.

The Pilot Plant exhibited a greater ability to remove DOC than the Torresdale Plant. This is exemplified by the large difference (725 ppb) in average DOC levels in the rapid sand filter effluents. This trend continued through the ozonation systems, where the average DOC difference increased to 825 ppb. The lesser capacity of the Torresdale Plant conventional treatment

TABLE 75 ESTIMATED BEDLIFE OF GAC FOR VARIOUS DOC CRITERIA[1]

Criterion: (Effluent Concentration)	Torresdale Plant				Pilot Plant			
	15 Min EBCT		30 Min EBCT		15 Min EBCT		30 Min EBCT	
	GAC	O_3/GAC	GAC	O_3/GAC	GAC	O_3/GAC	GAC	O_3/GAC
DOC = 0.5 ppm	38	57	88	144	76	84	152	213
1.0	69	148	216	246	146	225	296	NR
1.5	147	216	284	NR	258	NR	NR	NR
2.0	219	NR	NR	NR	NR	NR	NR	NR

[1] DOC Criterion based on 3-week running averages.

NR - No regeneration is required to maintain effluent levels below this criteria.

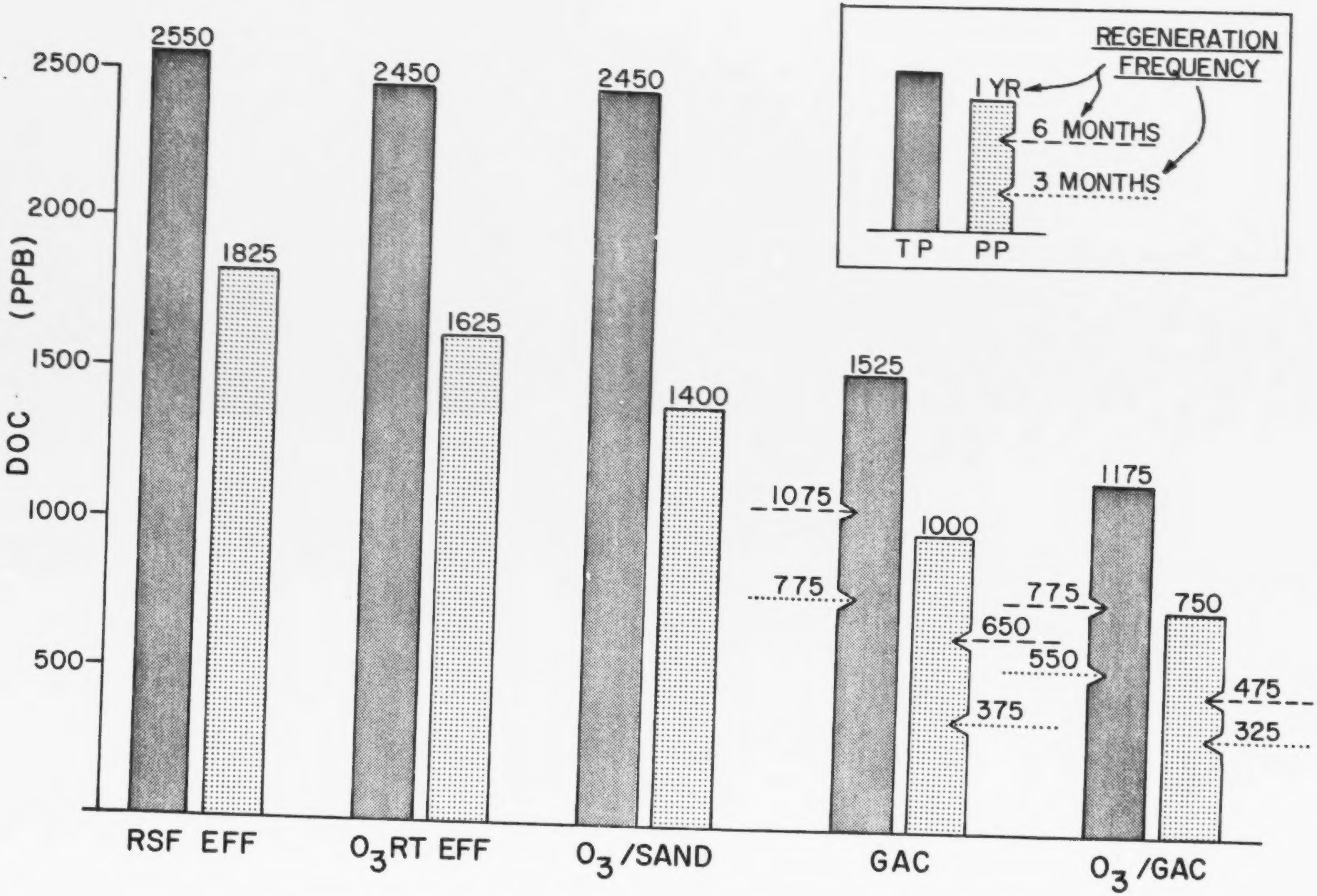

Figure 176. Summary of DOC levels through the treatment systems.

processes to remove DOC was due to a combination of less efficient flocculation/sedimentation and the absence of biological degradation (due to prechlorination). Through the Torresdale Plant ozone contactor, DOC oxidation was inhibited by the more resistant nature of the prechlorinated organics to further oxidation by ozone.

DOC levels in the Pilot Plant were further reduced through the sand bed following ozonation. All of the organics converted to readily biodegradable forms by ozonation were shown to be removed by biological activity in the sand bed. Although biodegradable organics were also likely to be produced through the Torresdale Plant ozone contactor, the residual chlorine present in the process water would prevent any biological activity on a sand bed. Increased DOC reductions of over 1000 ppb were thus obtained by improving the floc/sed process and by postponing chlorination until after ozonation and sand filtration.

Figure 176 also shows average DOC levels following GAC treatment (15 min EBCT) for both Torresdale and Pilot Plant systems. The expected DOC levels through the adsorption systems are shown for carbon regeneration frequencies of 3 months, 6 months, and 1 year. These DOC levels were derived by multiplying the average percent removal observed during the period until regeneration by the average influent concentration over the full year. This method helps normalize the variations in DOC influent concentrations over different time periods. For example, the GAC_{15}(TP) system had average influent and effluent concentrations of 2199 and 671 ppb DOC, respectively, during the first three months of system operation. By multiplying this average percent reduction across this contactor (69%) by the average annual influent concentration (2550 ppb), the average effluent value to be expected from this filter if the Torresdale Plant regenerated its GAC 4x/year becomes 775 ppb.

Improved DOC removal through the conventional treatment process (which reduced DOC loading onto the Pilot Plant adsorption system) also resulted in lower DOC concentrations in the GAC system effluents, regardless of regeneration frequency. For example, the Pilot Plant GAC system with a once per year regeneration cycle yields a better quality water (in terms of DOC) than the Torresdale Plant GAC system with six month regeneration frequencies. Of significance, the Pilot Plant ozone/sand system without GAC yields lower DOC levels than a typical GAC system established in the Torresdale Plant with regeneration of once/year. Thus, the importance of pretreatment on DOC levels in GAC effluents cannot be overstated.

Average DOC levels following the O_3/GAC treatment train are also presented in Figure 176. The O_3/GAC systems exhibited the same tendencies seen in the GAC system, although the average DOC levels for the preozonated systems were consistently lower. The O_3/GAC(TP) system with a 6 month regeneration frequency, for example, maintained DOC levels equal to that of a GAC(TP) system with regeneration every 3 months. Similar to the Torresdale Plant systems, the preozonated Pilot Plant system removes more DOC than the GAC(PP) system for equivalent carbon regeneration periods. Preozonation significantly improves the efficiency of the GAC process for removing DOC.

Mechanisms for TOC Removal--

Cumulative mass loading curves for DOC for the 15 minute adsorption systems are shown in Figures 177 and 178. Since some DOC breakthrough is observed from the start, the mass loading curves immediately fall short of 100% removal. However, there is a period of time at start-up when DOC removal is nearly equivalent in all systems, as is shown by the superimposition of one curve over another at DOC loadings below ≈ 30 mg/gm GAC for the Torresdale systems and ≈ 90 mg/gm GAC for the Pilot Plant systems. The difference between GAC and O_3/GAC systems began much more slowly for the Pilot Plant than the Torresdale Plant. This was due to the much longer duration of the initial breakthrough phase of the Pilot Plant systems (see Table 49). The point where the cumulative mass loading curves intersect the 50% removal lines represents the number of days a filter may remain in service and remove an average (over its service life) of 50% DOC. Alternatively, the point of intersection defines the regeneration cycle necessary for an entire plant whose GAC filters are replaced on a staggered timetable. The bed life of the 15 minute EBCT adsorption systems ranged from 248 to 406 days when this criteria was used.

The cumulative mass loading curves for the 15-minute EBCT Pilot Plant systems (GAC, O_3/GAC and O_3/Sand) are shown in Figure 179. In order to compare GAC versus sand, mass loading calculations are shown per contactor instead of per gram GAC, as they were previously. The curve representing the ozone/sand system is shown to remain along the x-axis until a loading of 300 grams DOC was applied. This corresponds to the first three months of the project when the ozone/sand system showed little capacity for DOC removal. Following this time, DOC removal through the sand bed was seen to remain relatively constant, averaging 19%.

For both the GAC_{15} and O_3/GAC_{15} systems, steady-state DOC removal was observed to begin after applied DOC loads of approximately 800 grams/contactor. For the GAC_{15} system, this steady-state removal averaged 20% (Table 51). Since there were no readily biodegradable organics in the influent to this system (all biodegradable organics were previously shown to have been removed through the conventional treatment processes of the Pilot Plant), all organic removal was attributed to adsorption. Whether additional adsorptive sites on the carbon became available due to slow adsorption kinetics (32,33) or biological reactivation (27,112,113) could not be determined from this data (the primacy of the slow adsorption kinetics theory will be shown in a later discussion on the minicolumn results).

Steady-state DOC removal averaged 36% through the O_3/GAC_{15}(PP) system (Table 51) and was observed to begin 5 weeks before the GAC_{15}. Since the minicolumn results demonstrate that the metabolic rate of the bacteria on GAC is equivalent to that on sand, the most that rapid organic biodegradation may account for DOC reductions through the O_3/GAC bed is equal to the 19% removal observed through the O_3/Sand system. Therefore, adsorption must account for at least half of the observed 36% steady-state DOC removal. For the GAC system applied with preozonated water, both adsorption and biodegradation appear to be significant mechanisms in the long-term, steady-state removal of DOC. Again, no determination could be made as to the mechanisms by which the adsorptive sites became available.

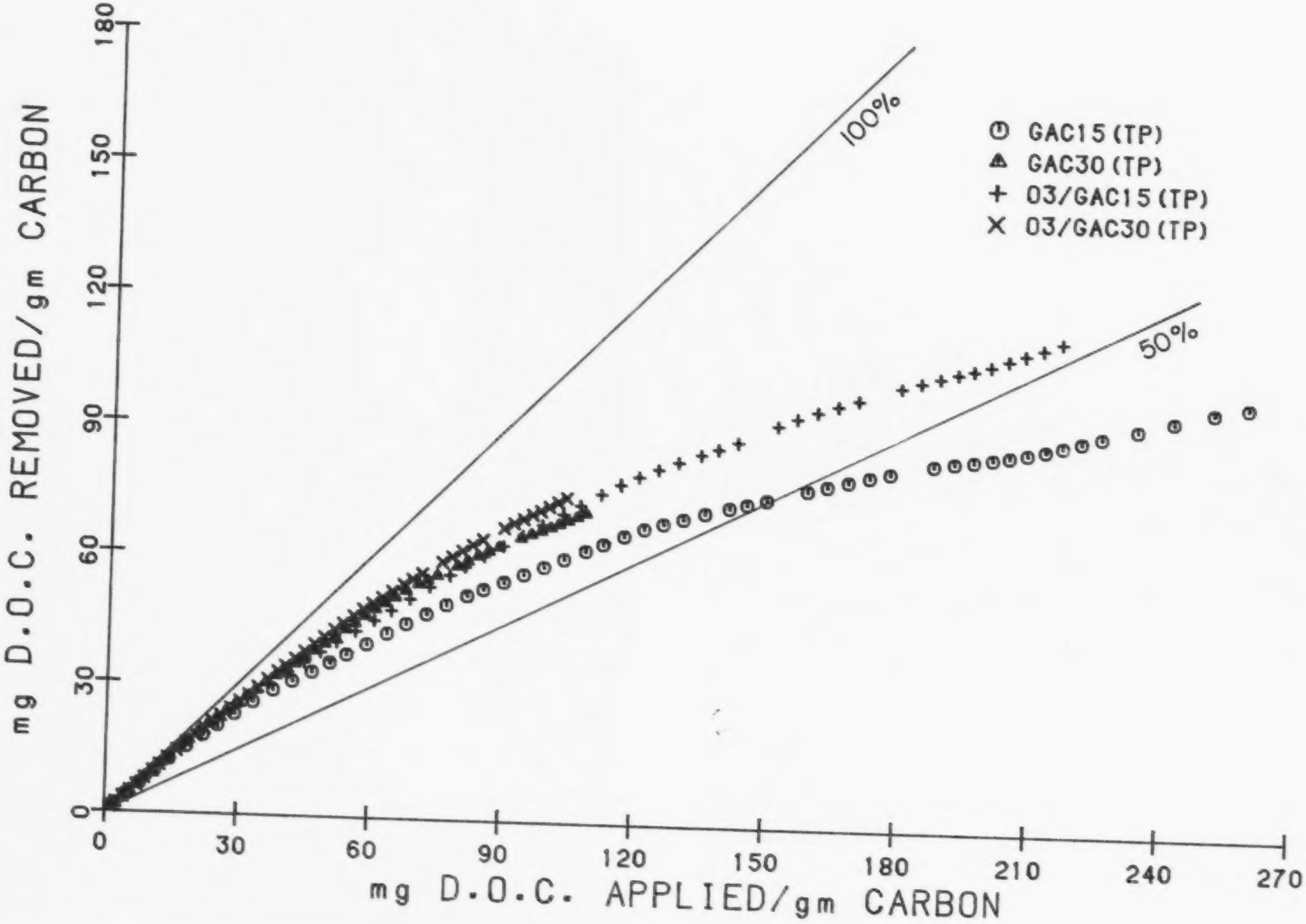

Figure 177. Cumulative mass loading curves of DOC through the Torresdale Plant adsorption systems.

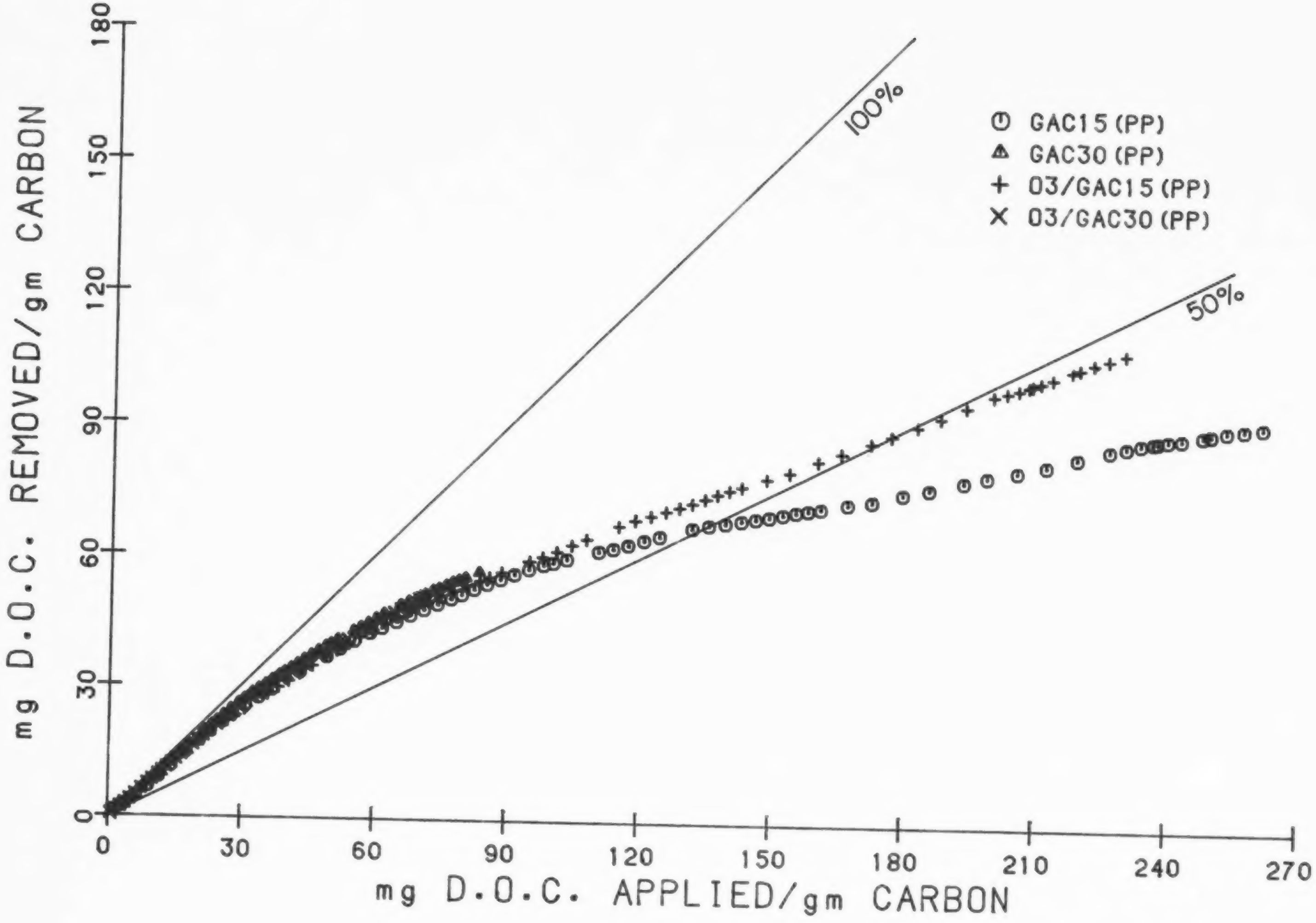

Figure 178. Cumulative mass loading curves of DOC through the Pilot Plant adsorption systems.

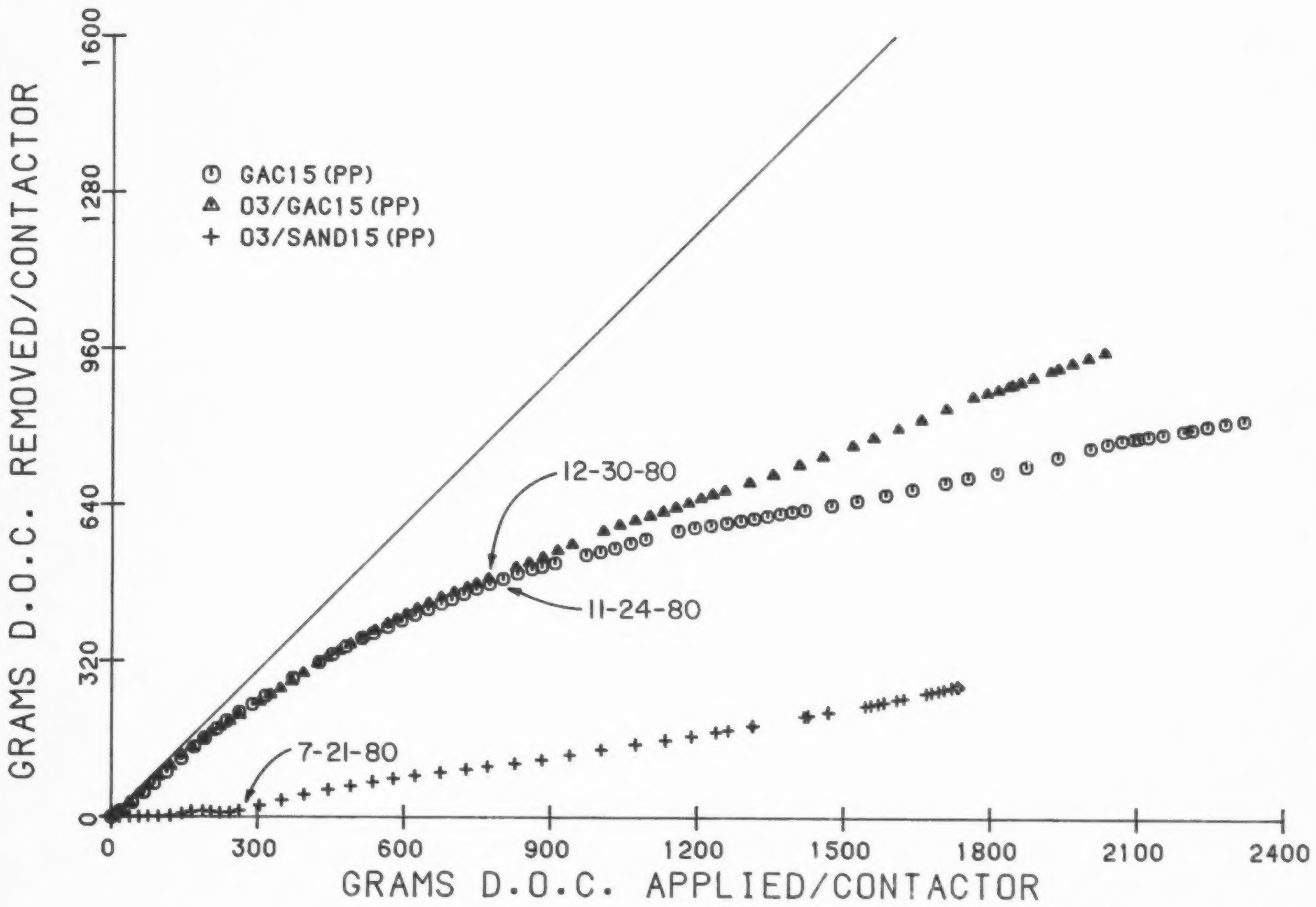

Figure 179. Cumulative mass loading curves of DOC for the Pilot Plant adsorption and sand systems (15 min. EBCT).

An additional removal of DOC by the combined, synergistic effects of adsorption followed by biodegradation of organics by acclimitized microbes was not observed from the data obtained during the O_3/GAC pilot-scale investigation. Therefore, the mechanism proposed to occur during the O_3/GAC process of biological activated carbon (27, 112, 113) apparently does not result in enhanced removal when compared to GAC alone.

Taste and Odor Criteria for GAC Regeneration--

The results of odor testing at several sites along the Torresdale and Pilot Plant treatment trains are shown in Table 76. Although only a limited number of samples were collected, sufficient data was available to make several generalizations. First, it appears that both conventional treatment trains produce a water of similar odor thresholds. The sources of these odors must be considered as different, however, since one type of odor results from chlorination while the other is primarily due to microbial activity.

The Torresdale ozonation system was not as effective as the Pilot Plant ozonation system in reducing the odor threshold value. This observation corresponds well with the conclusions made from the DOC, A254 and THMFP results, where it was concluded that prechlorination resulted in an increased resistance to further oxidation by ozone.

The O_3/GAC and the GAC systems all proved capable of removing odoriferous compounds from the process water. This reduction was nearly complete and appeared to be unaffected by the length of time the carbon bed remained in service, by the type of water applied, or by seasonal or temporal changes. However, while the GAC systems all proved capable of reducing the Threshold Odor Number, the use of ozone, either alone or in conjunction with GAC treatment, proved to be of little additional benefit in reducing the odor threshold.

Adsorptive Mechanisms in GAC Column Operation for Specific Organics--

In order to perform a comprehensive evaluation of differing adsorbents, both capacity and kinetic factors of adsorption and desorption of specific compounds are of importance. On a laboratory scale, single solute and competitive adsorption and desorption capacity and kinetic data can be easily obtained in the μg/l to mg/l concentration range. At present it is impossible to relate this information to real world systems where hundreds of compounds at μg/l to less than ng/l concentrations are present and a major portion of the TOC is a multicomponent high molecular weight mixture at the mg/l concentration level.

In real world situations, there are several phenomena observed during column operation which are important in the evaluation of adsorbent performance. Three phenomena of importance that are observed are breakthrough, exhaustion and the chromatographic effect:

- Breakthough occurs at the first appearance of substantial amounts of a compound in the effluent and indicates incomplete adsorption.

- Exhaustion occurs when influent and effluent concentrations of a com-

TABLE 76. ODOR[1] REDUCTIONS FROM O_3 and GAC TREATMENT

SAMPLING	PILOT PLANT				TORRESDALE PLANT			
DAY	RSF	O_3RT	O_3/GAC_{15}	GAC_{15}	RSF	O_3RT	O_3/GAC	GAC_{15}
68	17	5	2					
77	17	4	3					
82	24	4	1					
98	14	4	5					
112	17	8	0	6				
116	13	4	0	3				
126	13	8	4	3				
140	24	8	2	2				
147	24	8	3	2				
161	24	14	3	4				
168	24	8	3	3				
175	20	8	2	6				
182	17	8	3	3				
188	20	8	2	2				
196	17	8	2	2				
203					20	17	3	2
210	20	8	2	0				
217					24	17	2	4
229	24	13	2	3				
236					24	17	2	3
245	21	8	2	2				
250					24	17	4	4
266	24	8	2	4				
273					24	17	5	8
280	24	8	2	12				
285					24	17	2	4
292	24	17	3	8				
298					24	24	4	4
322	24	8	3	6				
329					24	17	4	4
336	24	8	3	4				
350					17	8	3	2
357	17	8	2	4				
378	4	4	2	6				
392	8	4	2	3				
399	17	8	2	4				
425	17	6	2	2				
440	17	8	1	4				
453	17	8	2	4				
475	17	6	2	2				
490	17	6	0	2				
496	17	8	0	2				

[1] Threshold Odor Number (TON)

pound become equal and indicates that, under the prevailing conditions, the solid and liquid phases are in adsorption/desorption equilibrium.

- A chromatographic effect is defined to have occurred when the effluent concentration of any compound is greater than its influent concentration at any point in time. It indicates that a new solid/liquid equilibrium is being reached.

The observed phenomena can change dramatically as a function of the interaction of column hydraulics and the chemical kinetics of adsorption and desorption. The mechanisms that produce the phenomena described above are competition and re-equilibrium.

- Competition involves the displacement to points further into the bed or into the effluent of a compound by another compound (or combination of compounds) which is rendered more highly adsorbed by either large intrinsic affinity for the solid phase or high concentration.

- Re-equilibrium may occur in a column whenever a compound decreases rapidly in the influent, leaving that adsorbed on the solid phase out of equilibrium with the liquid phase. Desorption will occur until a new equilibrium is struck.

These mechanisms indicate a new solid/liquid equilibrium is being reached.

A pure re-equilibrium process, driven only by the concentration gradients of the affected compound, probably exists only in the laboratory, since in an operational column all equilibria are struck among many competing compounds and the re-equilibrium desorption of any single compound will be "competitively aided". It is understood that all re-equilibrium mentioned in this report will include a competitive component also. Depending on the state of loading of the column, re-equilibrium may transfer part of the mass loading zone to points further into the bed or reject part of the compound into the effluent.

The mechanisms of displacement and re-equilibrium both can produce effluent concentrations higher than the influent concentrations of the affected species, the chromatographic effect.

Two other secondary mechanisms to be considered during long term use of an adsorptive column are the blockage of the openings to the adsorption sites by high molecular weight materials (e.g., humic substances, biological slimes, etc.) and chemical changes on the adsorbant surface (e.g., oxidation to carbonyl sites by chlorine or ozone). These mechanisms can cause a progressive loss of adsorptive capacity with time, slow the kinetics of adsorption and/or develop secondary adsorption sites on these materials.

Specific Organics- Criteria for GAC Regeneration--

Table 77 presents a summary of the breakthrough characteristics for DOC and THMFP and the volatile organics with the highest average concentration; $CHCl_3$, 1,2-DCP, acetone and dimethoxymethane. Tables 78 and 79 show the GAC breakthrough and chromatographic effects of all the volatile organics

TABLE 77. COMPARISON OF THE ORGANIC LOADS APPLIED TO THE VARIOUS ADSORPTION SYSTEMS

Parameter	GAC(PP)	O_3/GAC(PP)	GAC(TP)	O_3/GAC(TP)	O_3/SAND
DOC					
Applied (ug/L)					
- Average	1848	1625	2553	2440	1625
- Maximum	2442	2459	3131	2967	2459
SS Removal (%)	20	36	19	30	19
Days to 400 ug/L	73	73	32	36	NA
Days to 1.0 mg/L	146	225	69	148	NA
THMFP					
Applied (ug/L)					
- Average	119	100	99	105	100
- Maximum	156	148	164	214	148
SS Removal (%)	24		22	33	15
$CHCl_3$					
Applied (ug/L)					
- Average	4.3	2.8	73	46	2.8
- Maximum	43	26	163	110	26
100% Breakthrough (Days)	Spill event in Summer 1981		80	73	NA
Chromatographic Effect (weeks)	--	--	9-42; 45-47	9-42; 45-47	NA
1,2-DCP					
Applied (ug/L)					
- Average	4.5	3.0	6.1	4.8	3.0
- Maximum	19	16	24	22	16
100% Breakthrough (Days)	157	144	150	150	NA
Chromatographic Effect (Weeks)	34; 42-50	34; 42-50	22-25; 34-36; 42-49	22-25; 34-36; 42- 49	NA
Acetone					
Applied (ug/L)					
- Average	7.3	9.4	14.2	21	9.4
- Maximum	63	67	72	100	67
100% Breakthrough (Days)	NA	NA	NA	NA	NA
Chromatographic Effect (Weeks)	1-2;10-11;27;39	1;2;19;27	NA	NA	NA
Dimethoxymethane					
Applied (ug/L)					
- Average	4.1	2.3	3.7	3.1	2.3
- Maximum	19	13	17	14	13
100% Breakthrough (Days)	NA	NA	NA	NA	NA
Chromatographic Effect (Weeks)	7-10;15-21;36-49	7-8;10;19;33-35;43-50	6-19; 25-47	3;6-10;17-19;25-47	NA

TABLE 78. BREAKTHROUGH CHARACTERISTICS FOR SPECIFIC VOLATILE ORGANICS IN THE TORRESDALE PLANT

	Average Concentration Applied (ppb)		Weeks to Breakthrough				Chromatographic Effect (% of Time)	
			Initial		100%			
	GAC	O_3/GAC	GAC	O_3/GAC	GAC	O_3/GAC	GAC	O_3/GAC
Acetone	14.2	21.0	IMM	IMM				
Benzene	0.2	0.2	IMM	IMM	IMM	IMM	23	27
Chloroform	73.0	46.0	IMM	IMM	11	10	70	65
Methylene Chloride	0.3	0.3	IMM	IMM	4	2	44	34
Dichlorobromomethane	21.0	15.0	2	6	17	15	56	82
Dimethyoxymethane	3.7	3.1	3	3	3	3	67	75
Dibromochloromethane	5.5	4.8	9	10	33	33	63	88
1,2-Dichloropropane	6.1	4.8	9	13	33	21	75	50
1,2-Dichlorethane	1.4	1.3	13	9	14	14	72	72
1,1,1-Trichloroethane	0.2	0.1	14	17	14	17	28	50
1,1,2,2-Tetrachloroethylene	0.4	0.1	17	17	>50	>50	-	-
Carbon Tetrachloride	1.0	0.2	21	>50	21	>50	21	-
Bromoform	0.3	0.3	33	33	33	33	25	25
Trichloroethylene	0.4	0.4	35	42	>50	>50	-	-

TABLE 79. BREAKTHROUGH CHARACTERISTICS FOR SPECIFIC VOLATILE ORGANICS IN THE PILOT PLANT

Compound	Average Concentration Applied (ppb)		Weeks to Breakthrough				Chromatographic Effect (% of Time)	
			Initial		100%			
	GAC	O_3/GAC	GAC	O_3/GAC	GAC	O_3/GAC	GAC	O_3/GAC
Acetone	7.3	9.4	IMM	IMM				
Benzene	0.2	0.2	IMM	IMM	IMM	IMM	19	17
Chloroform	4.3	2.8	IMM	IMM				
Methylene Chloride	0.3	0.2	IMM	IMM	IMM	2	40	34
Dichlorobromomethane	1.0	0.8	2	IMM				
Dimethoxymethane	4.1	2.3	<7	<6	<7	<6	57	33
Dibromochloromethane	0.3	0.2	25	27				
1,2-Dichloropropane	4.5	3.0	17	14	22	22	60	44
1,2-Dichloroethane	1.2	1.0	14	14	22	16	60	61
1,1,1-Trichloroethane	0.2	0.1	19	34	20	34	19	31
1,1,2,2-Tetrachloroethylene	0.4	0.1	>50	>50	>50	>50	-	-
Carbon Tetrachloride	<0.1	<0.1	>50	>50	>50	>50	-	-
Bromoform	<0.1	<0.1	>50	>50				
Trichloroethylene	0.2	0.1	37	>50	44	>50	20	-

TABLE 80. ADSORPTION-DESORPTION OF TRACE ORGANICS[a] ON A GAC BED

Time Period	Mass Removal Rate	Competitive Effects	Location of Compounds in the GAC Column
1) Before Breakthrough	Constant	Minimal	Primarily at the top of the column
2) Initial to 100% Breakthrough (capacity of the column is attained)	Aproaches zero	Displacement maxima in the bed-little chromatographic effect	Uniformity throughout the column with displacement maxima
3) After 100% Breakthrough (capacity exhausted)	Varies (positive or negative)	Chromatographic effects	Increased concentration to the bottom of column

Based upon reference 173.

[a] Assume no biological changes or backwash

(C1-C10) whose average influent concentration is above the minimum detectable limit (0.1 ug/1). For the semivolatile organics (C8-C14) at the Pilot Plant and Torresdale Plant and the semivolatile organics (C14-C26) at the Pilot Plant, the breakthrough characteristics were shown previously in Figures 105, 107 and 108 for those organics with influents levels >0.2 ng/L (see Figures 60 and 61).

Previous pilot scale studies at Torresdale (1,34-38) have indicated that the influent water quality varied considerably in both the types of organics and their concentration. After breakthrough, the organic effluent concentrations also appeared highly variable. However, organics with lower boiling points generally appeared first in the effluent. The variability of the influent appeared to cause both competition and re-equilibration and subsequent sloughing of organics into the effluent. Competition of ug/l trace organics on GAC can be described in terms of three time periods using non-linear "frontal" chromatographic plate theory. Table 80 outlines the theoretical framework (173). Initial and 100% breakthrough and the chromatographic effect will be followed in this report.

A few laboratory studies on the competition between humic substances and trace organics have been completed. Trichlorophenol, methyl isoborneol, and geosmin showed competition with humics (111). In a recent study (174), competition of humics with CCl_4, dieldrin and PCBs was shown. No competition was noted for benzene or dichlorobenzene. Another recent study (175) using isotherm kenetics and small column studies showed that TOC levels of 3.3 mg/l did not compete with >100 ppb $CHCl_3$. As the $CHCl_3$ level decreased, a small amount of competition was noted. Thus, both laboratory studies (111,

174) and pilot plant studies (173) show that although competition can occur, the exact mechanism is compound and site specific.

Trihalomethanes-- Preozonation did not significantly alter the bedlife of the carbon adsorption systems when the criteria used for bedlife was based on limiting the effluent levels of the trihalomethanes. Figure 180 presents the percent breakthrough curves of chloroform (CHLO), dichlorobromomethane (DCBM), dibromochloromethane (DBCM), and 1,2-dichloropropane (DCP) for the Torresdale adsorption systems. Only the chlorinated, Torresdale Plant systems are shown since trihalomethane levels were minimal through the nonchlorinated, Pilot Plant systems (median concentration of 2.3 ppb). For these four halogenated compounds, no significant improvement in adsorption is observed when the applied water is preozonated.

It was surprising that there were no significant increases in bedlife when preozonation was employed, since the rate of organic loading (in terms of both, the general and specific organic parameters) was lower onto the O_3/GAC(TP) systems than onto the GAC(TP) systems. It was expected that the reduced loading of dissolved organic carbon (due to organic oxidation) would result in the availability of additional adsorptive sites on the carbon granules (i.e. less competitive adsorption) for specific volatile organics. Even more importantly, the reduced loading of volatile organic compounds themselves (due to aeration) was expected to at least increase the length of time the carbon beds were in service since the rate of GAC adsorption (ug/gm of GAC-day) was lowered. Instead, there appears to have been additional competition for the available adsorptive sites for the volatile organics and lower GAC adsorptive capacities.

Table 81 presents the carbon bedlife for the Torresdale adsorption systems. The criteria for bed exhaustion is based on various effluent limits for the trihalomethanes. The general trend to be observed from the table is that in nearly all cases the O_3/GAC systems reach exhaustion a few days sooner than the comparable GAC systems. One notable exception to this is the O_3/GAC_{15}(TP), which never exceeded the effluent limit of 100 ppb chloroform. This was due primarily to the aeration effect, which consistently held the influent chloroform levels to below 100 ppb and not to any increase in the adsorptive capacity of the GAC.

An interesting corollary to the above is that although the influent and effluent of the O_3/GAC_{15}(TP) system never exceeded 100 ppb, the O_3/GAC_{30}(TP) system (which receives O_3/GAC_{15} effluent as its influent) yielded effluents as high as 142 ppb. This is an example of the chromatographic effect which was exhibited by all of the systems investigated in this study. After the carbon bed reached exhaustion, there was a decrease in the influent concentration of the compound and a new equilibrium was apparently established between the water and solid phases. This new equilibrium resulted in a desorption of the compound from the carbon. Figure 86 shows the chromatographic effect for chloroform through the $GAC_{15}$and O_3/GAC_{15} systems. Once breakthrough was reached, the chromatographic effect was observed approximately 65% of the time, Table 78.

TABLE 81. CARBON BED LIFE FOR TRIHALOMETHANE REMOVAL[1]

CRITERION:	GAC_{15}(TP)	GAC_{30}(TP)	O_3/GAC_{15}(TP)	O_3/GAC_{30}(TP)
CHLO ≤ 1 ppb	35	84	32	81
≤ 10 ppb	51	94	44	88
≤ 100 ppb	78	112	—[2]	113
DCBM ≤ 1 ppb	69	129	63	124
≤ 10 ppb	92	178	90	160
DBCM ≤ 1 ppb	113	276	127	274

[1] Bed life based on 3-week moving averages in days.

[2] Highest effluent level recorded on Day 80 (CHLO=97.6 ppb).

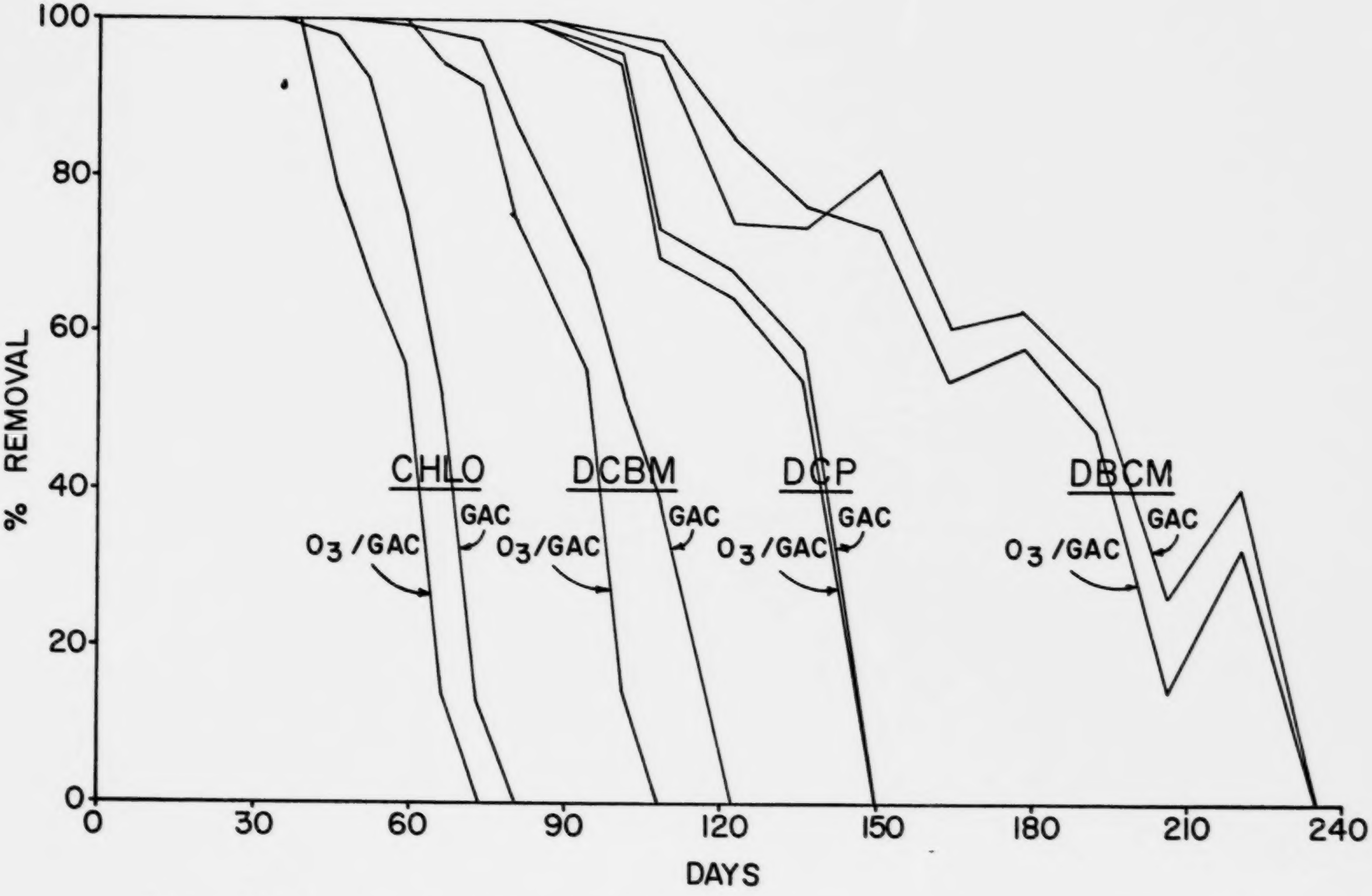

Figure 180. Comparative breakthrough of chloroform (CHLO), dichlorobromomethane (DCBM), dibromochloromethane (DBCM) and 1,2-dichloropropane (DCP).

The cumulative mass loading curves for chloroform (Figures 181-184) offer additional insight into the behavior of the adsorption systems. In all cases, the adsorption systems initially remove 100% of the chloroform. As bed exhaustion approaches, the mass loading curves diverge from the 45° line (the 100% removal line) and the maximum adsorptive capacity (MAC) of the carbon system (mg organic adsorbed/gm of carbon) is soon reached. Table 82 presents the observed and the theoretical MACs for CHLO, DCBM, and DBCM for the Torresdale Plant systems. The number of days the beds were in service before the MAC was reached is also shown. The maximum adsorptive capacities observed for the THMs were always less than the theoretical values derived from laboratory single-solute isotherm data. In fact, the observed MAC for chloroform is 44% below the theoretical value while, for DBCM, it is 80% less. Since the MAC is not reached until 100% breakthrough, this indicates that competitive adsorption is occurring during this time period (Table 80).

Table 82 shows that preozonation always resulted in reduced MACs. This may be due to the ozonation process producing additional low molecular weight organic compounds. While aeration reduces the volatile organic levels, oxidation increases them. The net effect is continued competition for the available adsorptive sites on the carbon. An alternative explanation centers upon the effect of the chloroform loading rate (ug/gm of GAC-Day) on the adsorptive capacities of the various GAC systems. From carbon adsorption isotherms of one-compound aqueous solutions (175), an increase in chloroform concentration from 10 to 50 PPB would result in a three-fold increase in adsorptive capacity. With an average reduction of 37% in chloroform levels through the Torresdale ozone contactor (see Table 73), therefore, it was not surprising to also find a decrease in the adsorptive capacity of the carbon for chloroform.

Following chloroform breakthrough, the GAC systems showed a chromatographic behavior: as the influent chloroform concentration dropped, desorption was observed; as the influent concentration rose, adsorption was again apparent (Tables 77 to 79). The net effect, as shown in Figures 181 to 184, was little to no change in the cumulative mass loading curves and a chromatographic effect for 70% of the time in the Torresdale GAC systems. However, an interesting phenomena was observed in the O_3/GAC_{15} systems. The cumulative mass loading of chloroform onto the carbon bed decreased from 0.83 mg/gm of GAC to near zero, indicating that over the one-year period of study, no net adsorption of chloroform had occurred. Again, this indicates that preozonation results in increased competition and/or re-equilibration of chloroform.

1,2-Dichloropropane-- Tables 77 to 79 show that except for the THMs, DCP has the highest influent concentration of any of the volatile organics. Table 83 presents GAC bed lives based on limiting DCP effluent concentrations to below 1 and 5 ppb. With these criteria, bedlife was typically increased through preozonation. The increases were small, however, and were probably the result of the reduced loading of DCP onto the O_3/GAC_{15} bed (due to stripping of DCP in the ozone contactors). Carbon bedlifes for the Pilot Plant adsorption systems were 1 to 2 months longer than the comparable Torresdale Plant systems. Here too, the effect of lower loadings of DCP may have been an important factor.

TABLE 82. MAXIMUM ADSORPTIVE CAPACITIES FOR TRIHALOMETHANES: OBSERVED (THEORETICAL)

PARAMETER:	GAC_{15}(TP)	GAC_{30}(TP)	O_3/GAC_{15}(TP)	O_3/GAC_{30}(TP)
CHLO				
MAC^1	1.36(2.41)^3	1.18(2.41)^3	0.83(1.73)^3	0.67(1.73)^3
DAY^1	73	115	66	101
DCBM				
MAC	0.60(0.75)	0.60(0.75)	0.38(0.61)	0.37(0.61)
DAY	150	220	101	192
DBCM				
MAC	0.29(0.82)	0.21(0.82)	0.24(0.78)	0.18(0.78)
DAY	235	284	220	291

[1] MAC= Maximum Adsorptive Capacities (mg/gm Carbon) - Observed (Theoretical)

[2] DAY= Day MAC is reached.

[3] Based upon the isotherm of Mueller et al (175) for HD-4000 GAC; All other isotherms based upon Dobbs and Cohen (176) for F-300 GAC.

TABLE 83. CARBON BED LIFE FOR DCP REMOVAL [1]

CRITERION:	GAC_{15}(TP)	GAC_{30}(TP)	O_3/GAC_{15}(TP)	O_3/GAC_{30}(TP)
DCP ≤ 1 ppb	109	215	113	194
≤ 5 ppb	203	323	272	316
	GAC_{15}(PP)	GAC_{30}(PP)	O_3/GAC_{15}(PP)	O_3/GAC_{30}(PP)
DCP ≤ 1 ppb	141	281	148	317
≤ 5 ppb	272	370	273	—[2]

[1] Bed Life based on 3-week moving averages.

[2] Highest effluent level recorded on Day 401 (DCP=4.0 ppb).

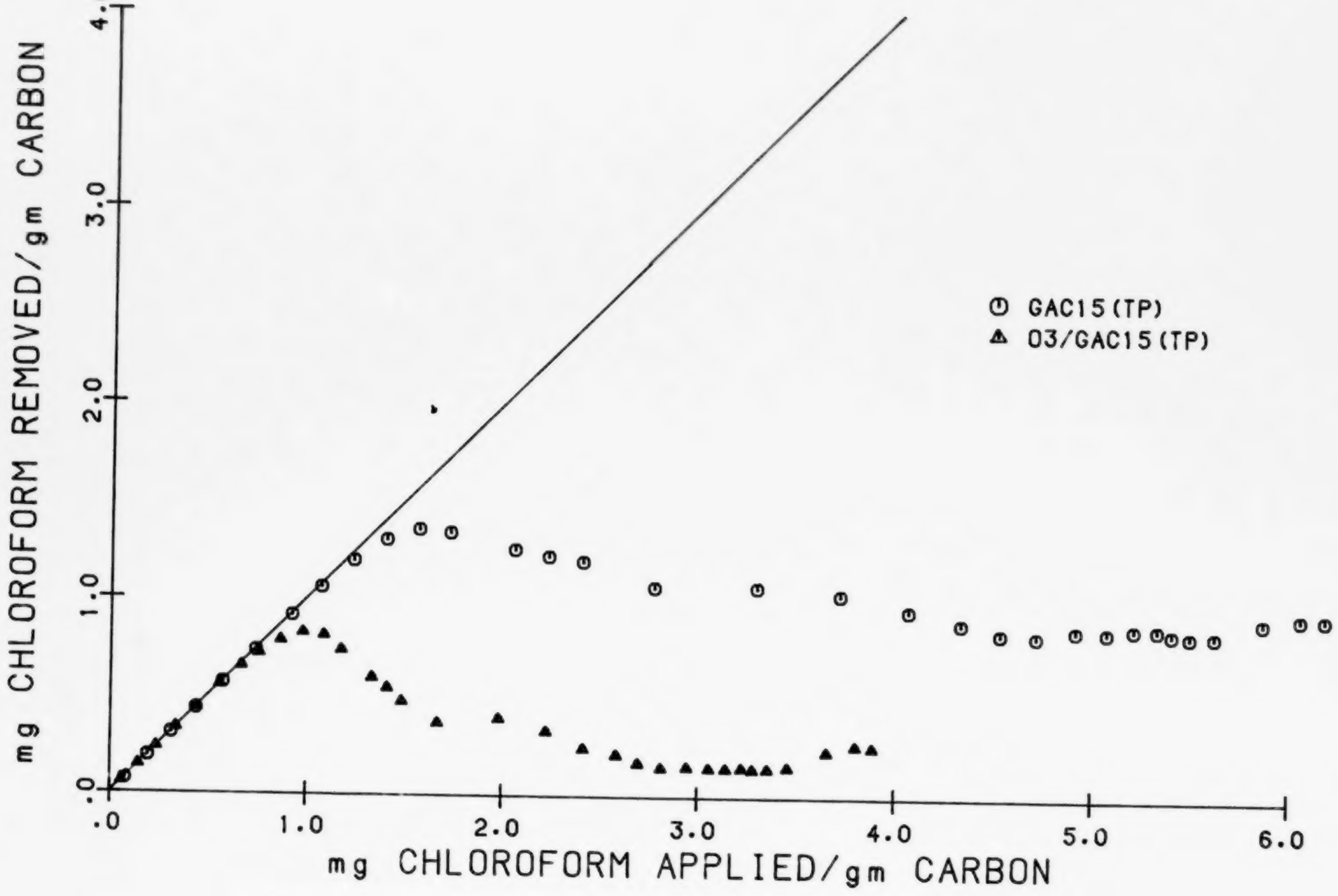

Figure 181. Cumulative mass loading curves of chloroform for the Torresdale Plant adsorption systems (15 min. EBCT).

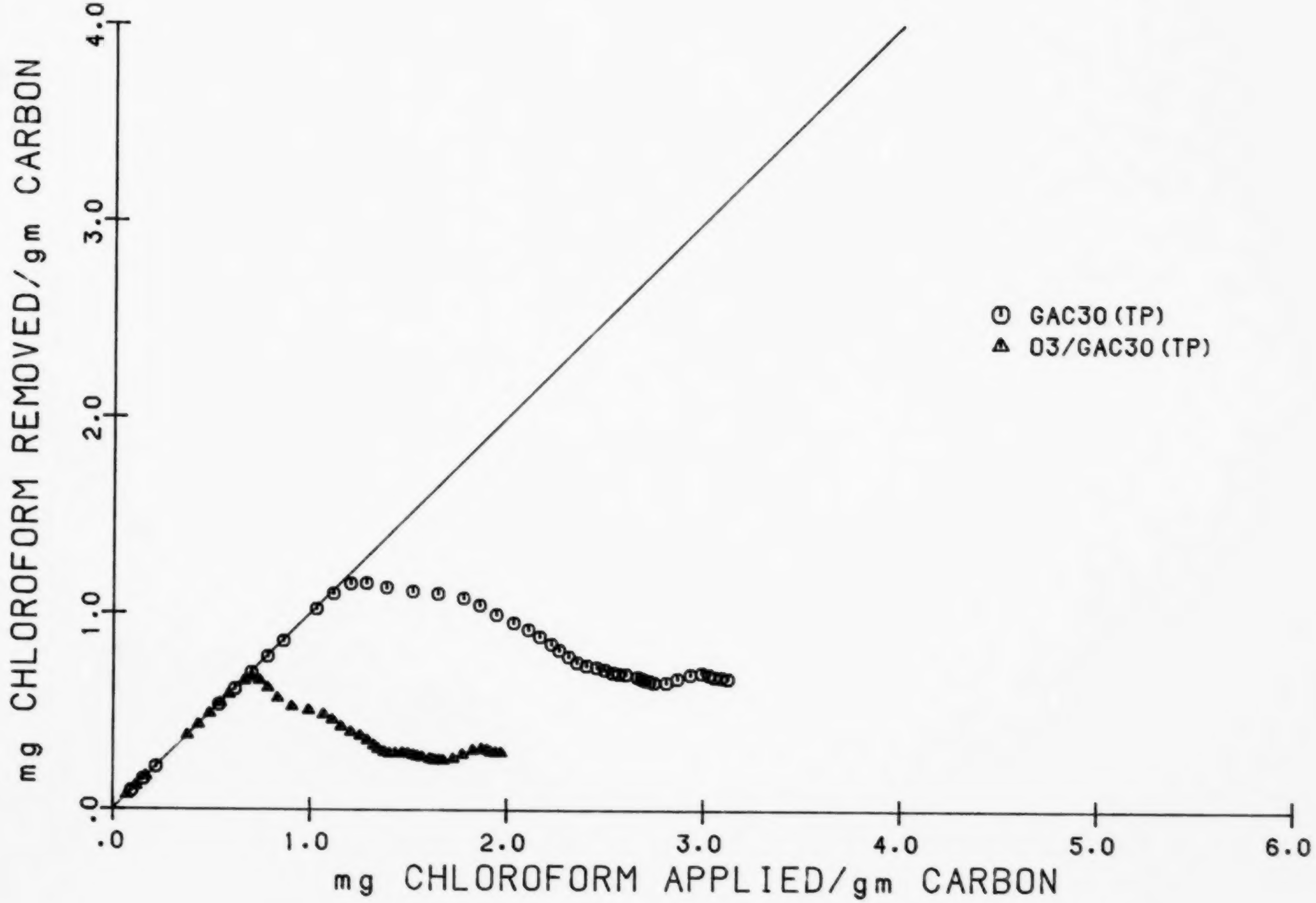

Figure 182. Cumulative mass loading curve of chloroform for the Torresdale Plant adsorption systems (30 min. EBCT).

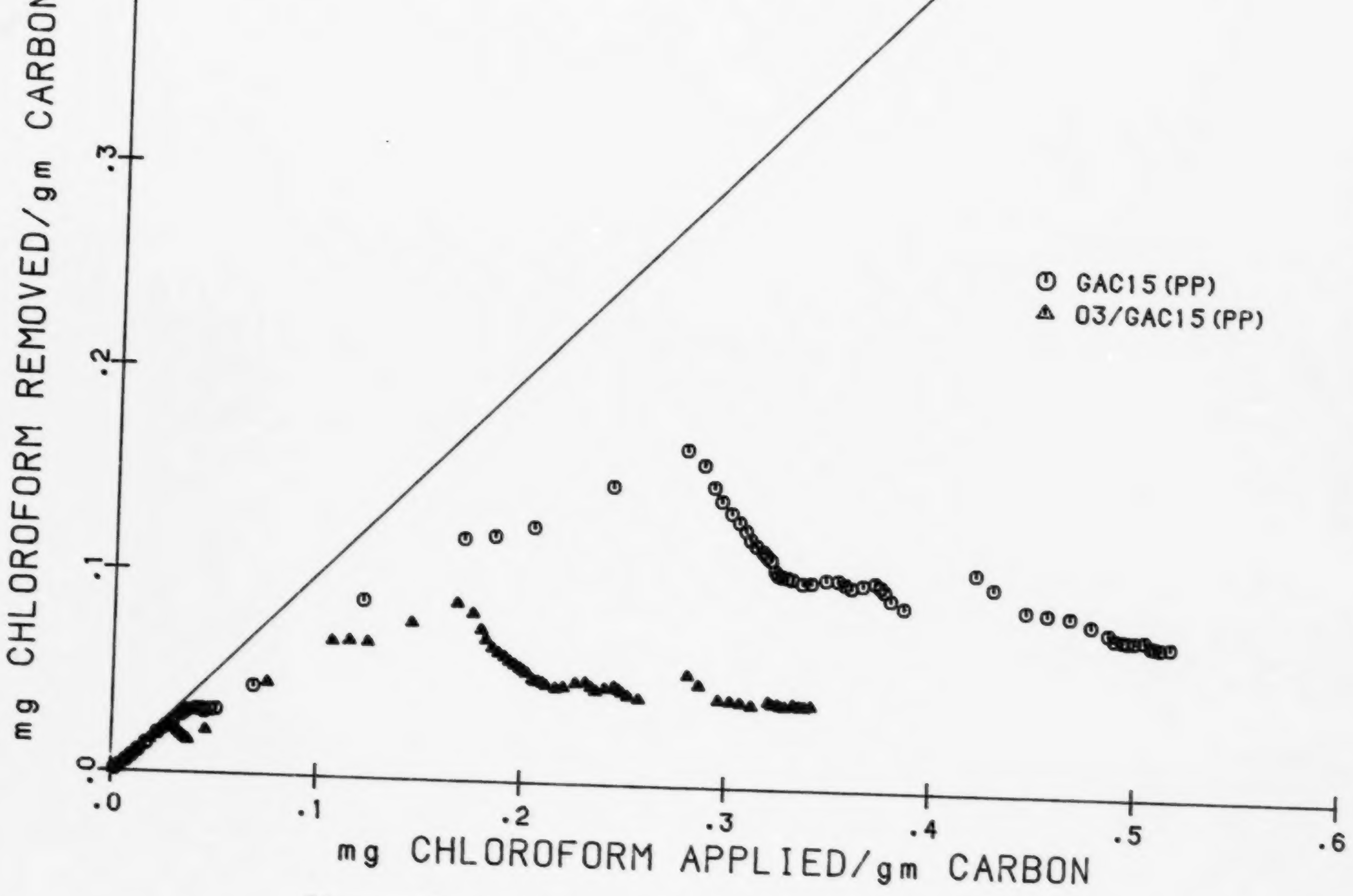

Figure 183. Cumulative mass loading curves of chloroform for the Pilot Plant adsorption systems (15 min. EBCT).

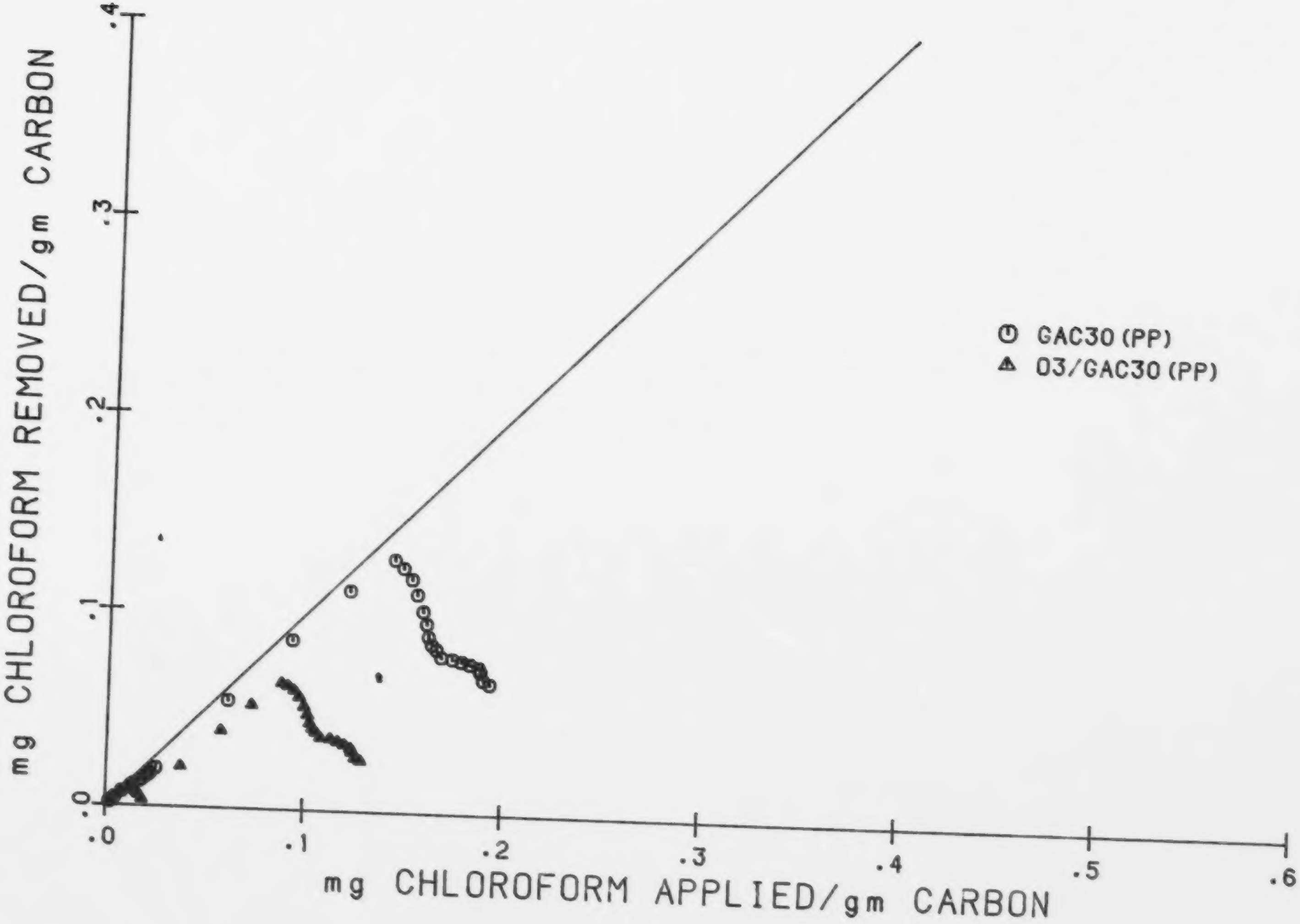

Figure 184. Cumulative mass loading curves of chloroform for the Pilot Plant adsorption systems (30 min. EBCT).

Table 84 presents the observed and theoretical adsorptive capacities of the GAC for DCP. Unlike for the THMs, the observed capacities of the GAC for DCP were nearly equivalent to the theoretical values obtained from single-solute isotherms. The commonalty of the days to the MAC appears due to a sudden drop in the influent DCP concentration which altered its equilibrium concentration. Again, the preozonated systems were not able to attain the same adsorptive capacities. It is interesting to note that the Pilot Plant systems did not attain MAC's which were as high as the comparable Torresdale systems. These results indicate that there is no competitive adsorption between the THM's and DCP. If there were, it would be expected that the Torresdale systems capacity for DCP would not be as great as that of the Pilot Plant. A chromatographic effect is observed 75% (GAC) and 50% (O_3/GAC) of the time at the Pilot Plant after 100% breakthrough is reached for DCP.

Volatile Organics -- Tables 78 and 79 presented breakthrough data for 14 specific volatile organic compounds measured by the purge and trap method. These compounds each had average concentrations of >0.1 ug/l. The occurrence of initial breakthrough was defined as the number of weeks until two or more consecutive samples showed effluent concentrations above the 0.1 ug/l detection limit. The occurrence of initial breakthrough ranged from immediate to > 50 weeks, the extent of the sample collection period.

The effect of preozonation on the time until initial breakthrough varied between compounds and between plants. For the Torresdale Plant, preozonation had no effect on the time to the initial observation of seven of the compounds in the effluent. Six compounds exhibited later breakthroughs and only one (1,2-DCE) reached breakthrough four weeks earlier when preozonation was used. Based on this criteria, therefore, preozonation resulted in an overall increase in the time until these specific volatile organics appeared in the GAC effluents.

For the Pilot Plant, preozonation resulted in the delay of breakthrough of three compounds and the early breakthrough of three others. Three reached breakthrough at the same time with and without preozonation. Thus, preozonation of the Pilot Plant water had no net effect on the time until specific volatile organics first appeared in its effluent.

Though this data indicates that it is more beneficial to preozonate Torresdale Plant effluent than Pilot Plant, an examination of the median time to initial breakthrough of volatile compounds shows preozonation to have no net effect on either plant effluent. Furthermore, the median time to initial breakthrough in the Torresdale Plant was 9 weeks, compared to 14 weeks for the Pilot Plant. Thus, conventional treatment via the Pilot Plant increased the median time to initial breakthrough while preozonation showed no significant effects. These observations hold even when these compounds affected by prechlorination are removed from the sample population (i.e. the four trihalomethanes and carbon tetrachloride).

Time until 100% breakthrough is also shown in Tables 78 and 79. Pilot Plant data for the four trihalomethanes is not presented because of abnormally high concentrations of the THMs during weeks 18 to 24 of the study. Inclusion of this data could result in the misinterpretation of the bedlife

TABLE 84. MAXIMUM ADSORPTIVE CAPACITIES FOR DCP - OBSERVED(THEORETICAL)

PARAMETER:	GAC_{15}(TP)	GAC_{30}(TP)	O_3/GAC_{15}(TP)	O_3/GAC_{30}(TP)
MAC[1]	0.26(0.27)[3]	0.22(0.27[3]	0.22(0.24)[3]	0.16(0.24)[3]
DAY[2]	291	305	305	305
	GAC_{15}(PP)	GAC_{30}(PP)	O_3/GAC_{15}(PP)	O_3/GAC_{30}(PP)
MAC	0.20(0.23)	N.A.[4]	0.13(0.18)	N.A.
DAY	291		291	

[1] MAC= Maximum Adsorptive Capacities (mg/gm Carbon) OBSERVED (THEORETICAL)

[2] DAY= Day MAC is reached.

[3] Theoretical MAC values based upon the isotherm data of Dobbs and Cohen (176) for F-300 GAC.

[4] NA= Data not available

expectancy of the Pilot Plant adsorption systems under the typical loading conditions outlined in Table 42. Data is also not presented for either plant for acetone. Acetone appears to be affected by the bacterial populations in the GAC columns and, thus, the extent of its removal due to adsorption is unclear. For the remaining compounds the results show 100% breakthrough occurring between 0 and >33 weeks after initial breakthrough. Again, the effect of preozonation varied from compound to compound and between plants. For the Torresdale Plant, time to 100% breakthrough for six compounds remained unchanged, while four reached breakthrough earlier and two later. Thus, based on a 100% breakthrough criteria, preozonation at Torresdale reduces GAC bedlife. This conclusion is the opposite to the one made above when the criteria was based upon initial breakthrough.

For the Pilot Plant, 100% breakthrough for four compounds remained unchanged, while three reached breakthrough later and only one earlier. Therefore, unlike the Torresdale Plant, preozonation resulted in increased GAC bedlife when this criteria was used. Again, this is not the same as the conclusion above, which was based upon initial breakthrough.

It is apparent that the conclusions drawn from the specific organic data are greatly dependent upon the criteria used. It is thus important to establish a criteria on which to best base GAC bedlife for specific organic removal. Another examination of Tables 78 and 79 shows that a chromatographic effect was observed for all compounds which reached 100% breakthrough within the time frame of the study period. Again, the "chromatographic effect" is the percentage of time after 100% breakthrough that each compound was observed in the effluent in concentrations exceeding those in the influent. The minimum percent of time for which a chromatographic effect was observed was for benzene (17%), while the greatest chromatographic effect was for dibromochloromethane (88%).

Maintaining GAC systems on-line beyond the 100% breakthrough of any of the specific organics listed on Tables 78 and 79 (for compounds with concentrations > 0.1 ppb) results in effluent levels above those in the influent. Any criteria established for reduction of these specific organic compounds, therefore, would best consider the time to 100% breakthrough. Whether this criteria is attained through the establishment of specific maximum contaminant levels (MCLs) for any of these compounds, or considers all as a group (those with concentrations >0.1 ppb) is dependent upon health considerations for the compounds under study.

Time to initial breakthrough is the important criteria if 100% removal of the volatile organic compound(s) is desired. However, if taste and odor, TOC, THMFP, or other parameters are the primary criteria and volatile organic reductions are an important, though secondary, concern, time to breakthrough is not as important as are the average effluent concentrations. In this case, ozonation is beneficial for the majority of the specific organic compounds mentioned above since their volatility will generally result in lower system effluent levels.

Semivolatile Organics -- GC profiles from the broad spectrum analysis (C8 to C26 hydrocarbons) of samples collected by the MRR method (>0.2 ng/l) were completed at each location for the first 17 weeks of system operation. A comparison of Figures 104 and 107 show that both, the sum of influent peak areas (C8 to C14) and number of peaks in the influent are lower for the Pilot Plant GAC contactors than the Torresdale Plant contactors. Yet during the first 7 weeks of GAC operation, the Torresdale and Pilot Plant removed most of the semivolatile, nonpolar compounds applied. Since the Torresdale influent had a greater concentration and number of semivolatiles, the mass loading of nonpolar compounds was greater onto the Torresdale GAC columns.

At Torresdale, through week 8, the GAC system was slightly more efficient than the O_3/GAC system. From weeks 8 to 17, the differences were not significant. Overall, O_3/GAC and GAC have minimal breakthrough differences over the 17 weeks of analysis. This is attributed to the preoxidation by chlorine presenting similar nonpolar semivolatiles in the influents to both adsorption systems.

At the Pilot Plant, both the GAC and O_3/GAC systems efficiently removed semivolatiles through week 10 (Figure 107). At this time, the O_3/GAC system began to show breakthrough of the lower molecular weight organics (C8 to C14), with breakthrough over the entire molecular weight range (C8 to C26) occurring after week 13. For the GAC system, no breakthrough was observed throughout the 17 week period of analysis. As was the case for the volatile organics, chromatographic effects were observed after breakthrough.

Ozonation before GAC at the Pilot Plant thus causes an earlier chromatographic effect for the semivolatiles. This can again be attributed to the production of lower molecular weight organics by ozonation causing increased loading (and competition) in the preozonated GAC bed. At the Torresdale Plant, prechlorination apparently resulted in little difference between the O_3/GAC vs GAC comparison for semivolatile organics, signifying the lesser effect of oxidation via ozonation in the chlorinated water.

Bacterial Populations in Granular Activated Carbon System

Most European potable water treatment systems employ GAC or ozonation or the two processes together. These treatment processes are used primarily to reduce the levels of organic compounds in the water and to improve the taste and odor of the final product (176-180). In the past 40 years, biological activity has been observed in these GAC and ozonated GAC systems (113, 119,181). However, only Klotz et al (118) in Germany did any extensive microbiological investigations. In the past few years the U.S. has become very interested in research into the microbiological aspects of advanced water treatment processes. This study examined both the populations and communities of bacteria in these GAC and Sand systems.

Although the growth of bacteria in carbon systems is well documented (113,118,119,181,182), the nature and extent of microbial colonization on the individual carbon particles has been speculative. Benedek (115) hypothesized that after initial colonization, bacteria continued to grow until there is a continuous layer of bacteria or a "bacterial film" covering the particle. Scanning electron microscopy (SEM) of carbon particles from past GAC studies (1) indicated that the carbon particles were sparsely populated with approximately 1% of the carbon surface covered with bacteria (Figure 143). Moreover, bacteria were found clumped together in the crevices and macropores and rarely found on the sheer surfaces of the carbon particle. This nonhomogeneous coverage of the carbon surface was also seen by Weber et al (117) in wastewater and Klotz et al (118) in potable water. Many of the bacteria were found attached to the carbon by pili. Some were found in the process of cell division.

Although amoebae were found associated with the carbon particles when examined under the compound microscope, there was no evidence of a protozoan community in the SEM micrographs. This indicates that the advanced ecosystems found in high substrate environments such as in wastewater did not develop in potable water GAC systems at Philadelphia. The SEM micrographs of clumped bacterial population centers and reproduction on the carbon particles also indicates that bacteria are reproducing in the columns and not merely being passively absorbed by the carbon from the influent waters.

The development of bacterial populations in the carbon columns was examined using a Soil Extract Agar Plate Count technique. Two multi-tap sand columns were used to monitor bacterial populations from the O_3/GAC at Torresdale and O_3/GAC at the Pilot Plant. Both GAC columns maintained a population of between 10^7 and 10^8 bacteria/g wet GAC (Figure 135) which is consistent with the results of Klotz et al (118) and Van der Kooij (119). However, an analysis of variance showed that the bacterial population in the O_3/GAC column at Torresdale was significantly greater than that of the O_3/GAC column even at the Pilot Plant although the influent bacterial levels to this GAC column were generally much lower. This can also be seen in Figure 139 to 142, where the cumulative distribution functions of the microbial populations of these columns are illustrated. A cumulative distribution function (CDF) is a way of representing the frequency distribution of a random variable. The CDF describes the proportion of the population for which the variate is less than a given value. These results were consistent with final bacterial populations found in the O_3/GAC(TP) and O_3/GAC(PP) columns at breakdown.

As shown in Figure 135, the bacterial population at the top of the O_3/GAC(TP) column was almost twice that of the unchlorinated O_3/GAC(PP) column. This marked population difference between the two columns may be due to the greater biodegradable substrate levels in the influent of the chlorinated column at the Torresdale plant. Little or no bacterial growth was allowed to develop in the prechlorinated system, therefore, little if any of the biodegradable organics would be removed from the water before it entered the column. In the nonchlorinated pretreatment system of the Pilot Plant which supplied the O_3/GAC column, the readily biodegradable organics were reduced by the bacterial populations prior to the column. This conclusion was supported by the large bacterial populations found in the raw water basin (~ 300,000 bacteria/mL) and the clarifier sludge mat (1,400,000 bacteria/mL). Therefore it can be concluded that the biodegradable organics content in the influent to the O_3/GAC(PP) column was smaller than that in the O_3/GAC(TP) column.

Chlorination of influent water reduced the bacterial populations at the top of the GAC columns. This can be seen in Figure 135, where populations in the top layer of the GAC(TP) column were 10 to 100 times lower than those of any other column. Ozonation of the chlorinated influent water eliminated this effect. Bacterial populations in the GAC(PP) column were also found to be significantly lower than those in the O_3/GAC column. This can be explained by the increased utilizable substrate in the ozonated influent waters. This same condition (increased bacterial populations with ozonated influents) was also seen in the O_3/GAC and GAC columns at the Torresdale Plant (Figure 135).

Two sucessive O_3/Sand columns each with 15 min. EBCT were also set up in the Pilot Plant to determine the capability of a sand system to remove biodegradable TOC. TOC removal from these columns averaged 19% after 3 months of Pilot Plant operations (Figure 109). This can be attributed to the bacterial activity on the sand removing organics from the water. Although no record of the development of the bacterial populations on the sand is available, population densities at the top of the O_3/Sand$_{30}$(PP) column at breakdown were 10^7 bacteria/g sand. This was lower than population densities found at the top of the O_3/GAC$_{30}$(PP) column but very similar to levels found in the rest of that column. Sand column effluent bacterial levels (Figure 133), were similar to those recorded in the O_3/GAC(PP) column effluents.

In addition to determining the densities of microorganisms in the GAC and Sand columns and their effluents, all Total Coliforms and the dominant AFAH bacteria were isolated and identified. Most of the Total Coliform group were destroyed in the pretreatment processes, especially in the Torresdale system. Klebsiella pneumonia, Klebsiella oxytaca, Enterobacter cloacae and Citrobacter freundii were most resistent to the Pilot Plant pretreatment process, most likely beacuse Klebsiella and Enterobacter are capable of encapsulation which makes them more resistent to environmental stresses. Ozonation effectively eliminated most of these organisms. However, even when ozonation did not precede the GAC columns, such as in GAC$_{15,30}$(PP), 75% of the coliform were removed through the columns. Occassionally *Klebsiella oxytaca* and *Citrobacter freundii* were found in the sand and GAC effluents and more rarely in the ozonated GAC effluents. Minimal post chlorination of the GAC column effluents will effectively eliminate any coliform eminating from the columns.

AFAH bacteria were also effectively removed by the Torresdale pretreatment process. *Bacillus* and *Flavobacterium* species were the only organisms consistently found in the RSF effluent and the Torresdale ozone retention tank. Obviously, environmental restraints limited the community diversity at these locations to those forms most resistent to the effects of chlorine. The bacterial population in the Pilot Plant Ozone Retention Tank was more diverse and was composed of *Bacillus*, *Flavobacterium*, *Pseudomonas* and *Alcaligenes* species. It should be noted here that although the ozonator effluent contained few bacteria, a bacterial community did develop in this retention tank with levels that averaged 10^2 bacteria/ml. Once the influent waters entered the GAC columns the negative effects of chlorine and ozonation were lost and any bacteria that had somehow survived these processes found a more favorable environment as can be seen from the rapid increases in bacterial populations in the O_3/GAC columns at Torresdale (Figure 128). Although the chlorinated and nonchlorinated influent bacterial populations differed in species composition, the bacterial communities which developed on the carbon and in the column effluents was very similar. *Pseudomonas* and *Flavobacterium* species dominated the communities throughout the year as can be seen in Figures 130 and 137. *Acinetobacter*, *Alcaligenes* and *Bacillus* species were also common at certain times of the year. *Acinetobacter* and *Alcaligenes* species were more common in the early spring. This correlates with their ability to grow at lower temperatures. Whereas, *Bacillus* species were found predominantly in late summer and fall when temperatures reached 20°C for above. This change in community composition therefore can be linked with temperature changes in the surrounding environment. A corresponding relationship between bacterial species composition and temperature was also observed in the river community.

As noted above, the community diversity of the six columns was rather limited. Two groups of organisms, *Pseudomonas* and *Flavobacterium* dominated the community. Fourteen species of *Pseudomonas* were identified. The Genus *Pseudomonas* includes a large group of very common and widely distributed organisms found in soil, fresh and marine waters and sewage. This group is characterized by its ability to utilize many different organic compounds including hydrocarbons and pesticides as a source of carbon and energy under aerobic conditions. The *Flavobacterium* group which was also dominant in this community, is also a common soil and water saprophyte. However, it is more limited in its decomposition abilities than the *Pseudomonads*. Five species of this group were isolated. *Alcaligenes* and *Acinetobacter* were common in this community in the spring. Three species of *Alcaligenes* and two species of *Acinetobacter* were identified. Several species of *Bacillus* which was common in the summer and fall were isolated, however, they were not identified to the species level. The various species of *Pseudomonads*, *Flavobacterium*, *Bacillus* and others which were identified in this study can be found in Table 64. Occasionally other types of bacteria were also found in these communities, however, they were never common. Included in this smaller group of occasional community members were Azotobacter, Achromobacter, Cytophaga and Micrococcus bacteria. All of the AFAH bacteria isolated and identified in this study are common soil and water organisms. Most of them have been recovered in other GAC studies (118,119,121, 183)

Chlorination studies conducted during this project have shown that the bacterial populations in the column effluents are effectively eliminated by chlorination (Tables 68 and 69). However, since species of Flavobacterium and Bacillus bacteria have been shown to be more resistent to chlorine than other types of bacteria, a more vigorous distribution sampling program would be instituted when GAC is used in the treatment process to ensure that these organisms do not get established in the distribution system.

Bacterial Growth Characteristics

Attachment of microorganisms to the surfaces of GAC has been clearly shown (117), however the mechanisms have not been widely investigated. In fact little consideration has been given to the actual determination of growth of bacterial populations on GAC columns. Cairo *et al* (1) has tried to relate the effluent bacterial density data to the bacterial growth rate in the GAC columns. It was assumed that during initial colonization, the bacteria were in exponential growth and had not reached equilibrium. The "young cells" were easily washed off but were later replaced by more "mature" stable cells, thus reducing sloughing (9).

The approach taken in this study was to consider the GAC column as a "black box" in which the microogranisms function for individual maintenance and production of new cells at the expense of energy and carbon sources entering the column. A mass balance approach was used to assess bacterial production within the columns as follows:

$$\text{Increase} = \text{Growth} - (\text{Washout} - \text{Input}) \qquad 1.$$

This modified equation considers the bacteria at all locations, and not just within the contactor or effluent.

Results of the enumeration studies are similar to those reported elsewhere (1,116,118), that is, microbial populations on the GAC itself were several orders of magnitude higher than influent and effluent concentrations. Exceptions to these generally observed results were (1) influent concentrations were higher than normally observed and (2) higher influent than effluent concentrations at GAC contactor steady state were measured. The higher than normal influent bacterial densities may be the result of holding the water in a retention tank for 30 minutes, to dissipate ozone, prior to passage to the GAC columns and/or a sand prefilter between the GAC contactor influent and the retention tank.

Using the mass balance approach the observed responses varied from net growth to, in pseudosteady state, a significant loss of bacteria across the GAC columns (Figure 185). The data demonstrate that even though maintenance of large populations of bacteria on GAC was observed, a significant loss of

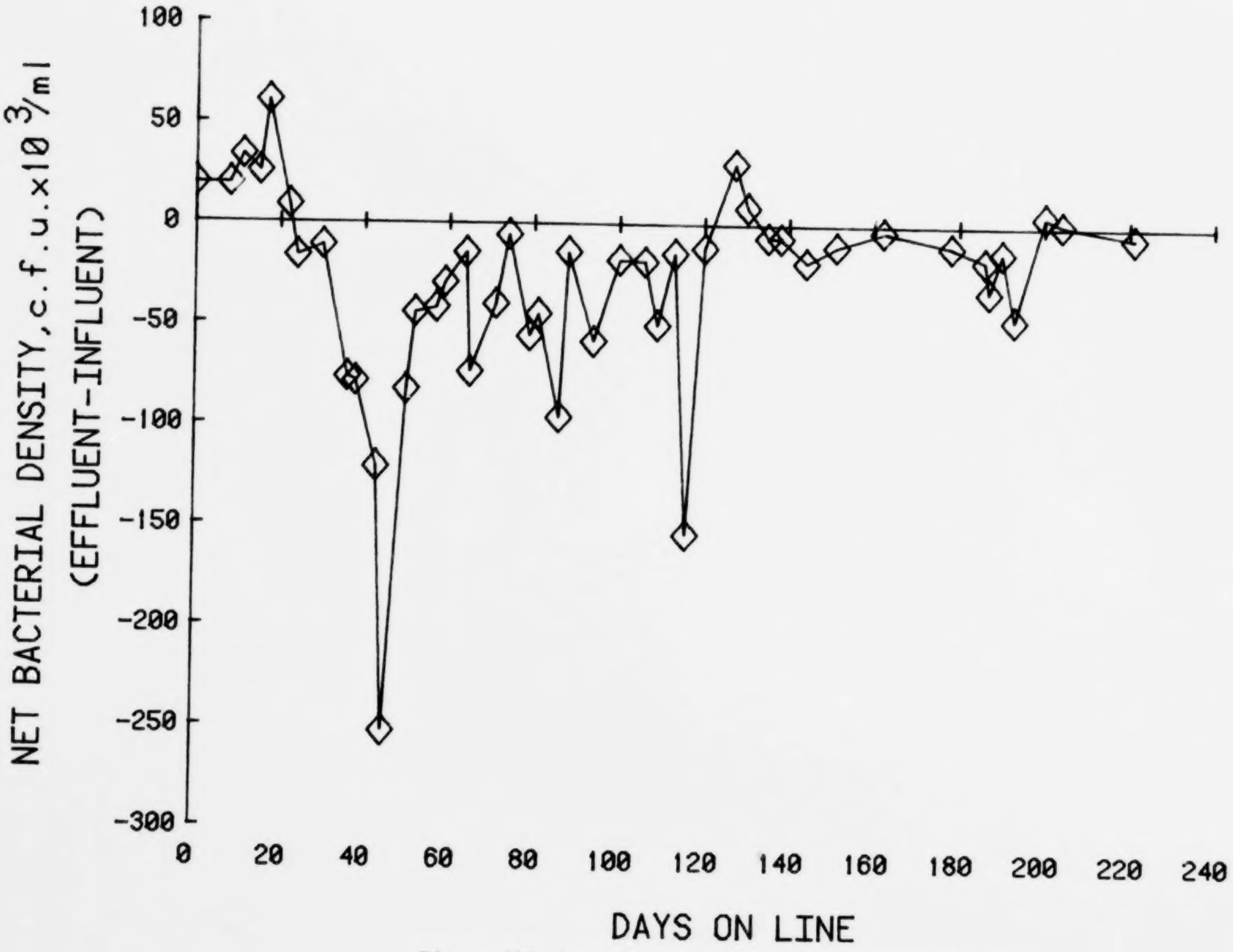

Figure 185. Mass Balance of Bacteria - Mini-Columns.

organisms across the columns may occur. This loss may be the result of most of the substrate being used for maintenance requirements of the GAC column populations.

The typical sigmoidal growth curves observed in this study for GAC bacterial densities have been previously attributed to exponential growth followed by decreased growth as the environment begins to limit growth (1). However, population doubling, or turnover times on GAC, have not been measured. To test the above hypothesis, data collected from a filtered GAC column (A) and a nonfiltered GAC column (B) were applied to two models for calculating bacterial doubling time. The three models used were:

The net change in densities of organisms in the contactor (X) with time can be determined as in equation 1. which can be rewritten as follows:

$$dX/dt = X - D\,(Xe - Xi) \qquad 2.$$

Where X is the bacterial density on the carbon, Xe is the effluent density, Xi is the influent density and D is the dilution rate. Since D = Q/V;

$$dX/dt = \mu X - Q/V(Xe - Xi) \qquad 3.$$

Where Q is the flow rate, V is the Volume of the contactor and μ is the growth rate. In pseudosteady state:

$$dX/dt = 0;\ \therefore\ \mu X = Q(Xe - Xi) \qquad 4.$$

or

$$\mu = \frac{Q(Xe - Xi)}{VX} \quad \text{or} \quad \mu = \frac{Q(Xe)}{VX} \qquad 5.$$

• When Xi is negligible when compared to Xe, it may be omitted.

This equation is for completely mixed systems rather than attached growth; however, the density of bacteria on the GAC did not vary dramatically with depth in the contactors, therefore the completely mixed model is reasonable. In steady state the growth rate therefore can be easily calculated.

Prior to steady state, growth rate can be model calculated by the mass balance equation (2):

$$X = \frac{(Xe - Xi)Q}{V}^{e\mu t} - \frac{(Xe - Xi)Q}{V}$$

Where: X = GAC bacterial concentration
Xe = effluent bacterial density
Xi = influent bacterial density
Q = flow rate
μ = specific rate
t = time

This model is not applicable to the steady state mode.

These calculations were performed for the filtered and nonfiltered 25 inch GAC contactors. No statistical difference was found in growth rate therefore the average of the two are presented (Table 85). The results indicate a decrease in the growth rate of bacteria on the column until pseudosteady state is attained. During pseudosteady state, fluctuations in growth rate occur with the mean population doubling time being six days. Total bacterial production/ml of water passing through the column during this period was found to be relatively constant and organic carbon requirements for this production were calculated (185, 186) to be less than 10 µg Glucose equivalent C per liter. These calculations however do not consider carbon requirements for the maintenance of GAC bacterial populations. This question will be considered later.

GAC bacterial densities were found to comprise 2% of the total production for the first 9 days and 54% after 27 days. After 66 days bacterial densities found on the GAC were calculated to comprise of only 9% of the total bacteria produced. Bacterial growth is ideally exponential because the size of the population is related to an exponential function to the base 2 (187) and the growth rate is determined by the steady state nutrient concentration. In a continuous culture apparatus with complete mixing, the constancy of the population size and growth rate is maintained by the steady state concentration of the limiting nutrient which is determined by the flow rate of fresh medium (188). In these GAC contactors, bacterial production remains fairly constant, but because of the adsorptive capabilities of the GAC, the population within the contactor continues to increase. Since the growth rate or doubling time is a function of the initial bacterial concentration, as the GAC bacterial concentration increases with time and the production remains constant the growth rate will decline as shown on Table 85. This constant production is indicative of nutrient limited growth conditions and the typical sigmoidal growth curve observed on the GAC appears to be the result of accumulation rather than increased exponential growth.

TABLE 85. GROWTH RATE (µ) AND BACTERIAL PRODUCTION ON THE GAC MINICOLUMNS

DAYS	Growth Rate $(\mu)h^{-1}$ Eqn. 3	Growth Rate $(\mu)h^{-1}$ Eqn. 6	Bacteria x 10^4 produced /ml of H_2O
4	0.5*	0.14	1.2
9	7.1×10^{-2}*	7.1×10^{-2}	3.7
17	3.1×10^{-3}*	1.4×10^{-2}	8.0
27	1.7×10^{-3}*	8.6×10^{-2}	5.5
36	9.2×10^{-3}	5.4×10^{-2}*	2.0
41	3.6×10^{-3}	5.1×10^{-2}*	8.2
48	6.8×10^{-3}	3.6×10^{-2}*	-0.09
55	2.3×10^{-3}	3.7×10^{-2}*	5.7
66	6.4×10^{-3}	2.5×10^{-2}*	-1.1

- net death.

* model not considered to fit conditions.

In pseudosteady state when GAC bacterial concentrations and total bacterial production are constant, the doubling time and residence time should remain constant. During pseudosteady state conditions (day 27 to day 66), the average bacterial production (2.95×10^4 c.f.u./ml) was found to fluctuate sometimes showing a net loss of bacteria. These fluctuations were found to coincide with fluctuations in bacterial doubling times or residence time in the GAC contactor. Average pseudosteady state values for doubling time were approximately 6 days. These fluctuations in growth rate (and residence time) are the result of fluctuations in bacterial densitites of the GAC contactors and are probably a function of influent nutrient concentration and equilibrium phenomena.

The long term doubling time of bacteria "appears" to be more closely tied to the influent and effluent bacterial densities than carbon surface bacterial concentration. Fluctuations in doubling time are calculated when fluctuations are observed in either or both of the aforementioned measurements. A common observation of bacterial densities both on carbon and in the effluent is low initial counts, rising to a maximum and then declining to a pseudosteady state condition (1, 116). This type of data versus time generates a plot such as Figure 186, although actual field data has a great deal of scatter. During the increasing portion, there is an apparent high growth rate, hence production is proposed (1, 116), which levels off during the time surrounding the maximum cfu/ml and then declines again during steady state. These observations have been previously credited to rapid growth followed by bacterial sloughing as the population stabilizes (116). An alternate explanation is presented here which takes into account the adsorptive properties of GAC and allows the bacterial production to be a function only of the limiting nutrient and does not require bacterial sloughing to occur.

Consider the adsorptive phenomenom occurring when the column is started up. There are essentially no bacteria on the carbon and adsorption is only a function of the influent substrate concentration. The driving force for adsorption is quite high and bacteria are not competing for the substrate. This is shown in Figure 187 as the initial condition on an isotherm-type representation. Under this condition, the driving force for adsorption would cause a surface concentration of q_{e1} as shown. After bacterial densities increase, whether by growth or adsorption of bacteria, substrate on which bacteria can act is removed from the liquid phase concentration, and the driving force is for a surface concentration of q_{e2}. These represent initial and final (steady state) boundary conditions. During the transition from C_{e1} to C_{e2} however, substrate adsorbed under the initial condition may desorb to the liquid phase. Thus more substrate is available to the bacteria than that in the influent. Only a limited amount of substrate could be stored by the GAC; therefore, the maximum bacterial densities do not persist. After the surface concentration is in equilibrium with the (bacterially controlled) final liquid phase concentration, growth of bacteria is limited to that amount supportable on the influent substrate without the aid of stored substrate.

In long term pilot plant experiments, during GAC pseudosteady state, it seems apparent that insufficient substrate was available for bacterial growth

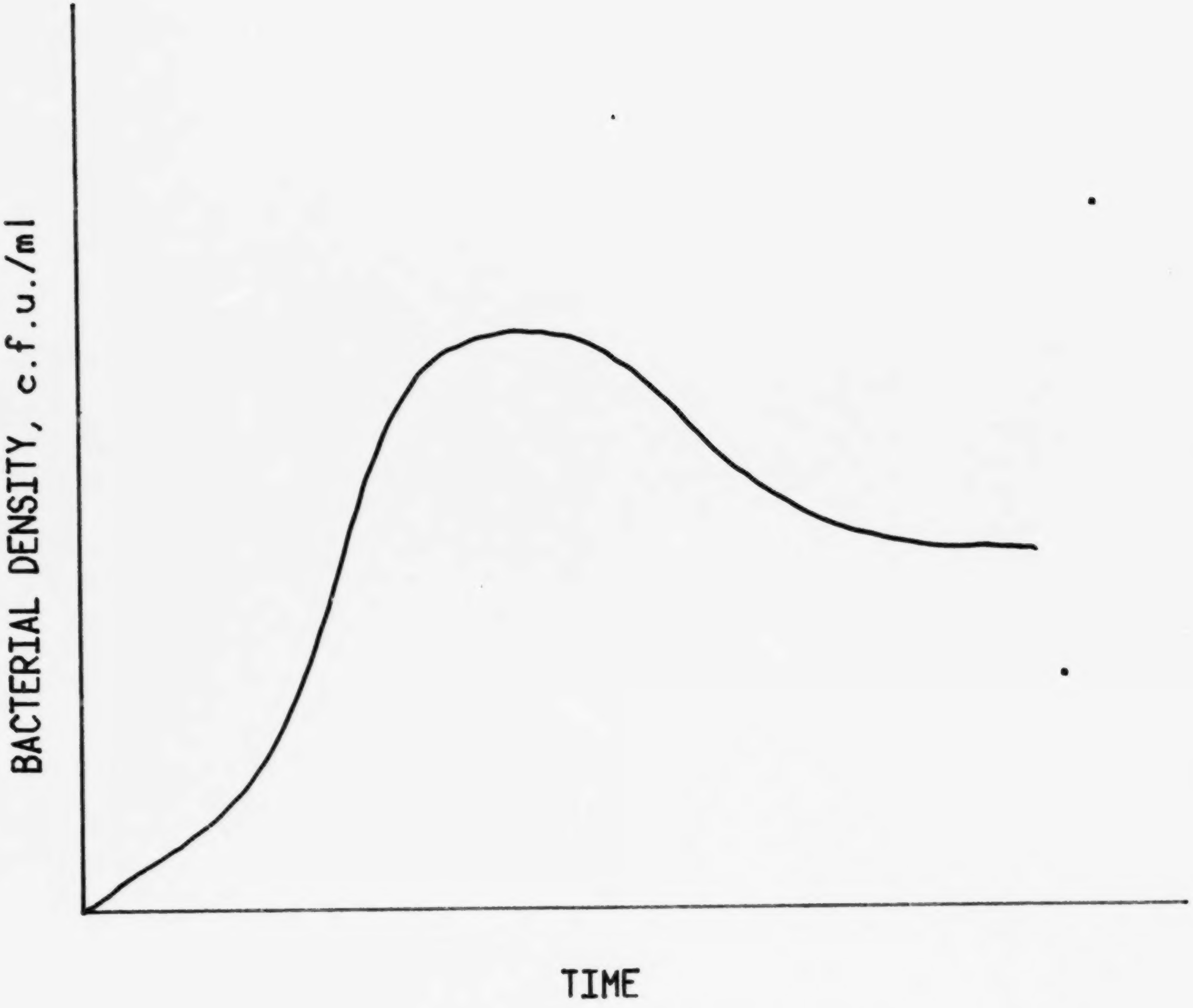

Figure 186. Typical GAC Effluent Bacterial Density.

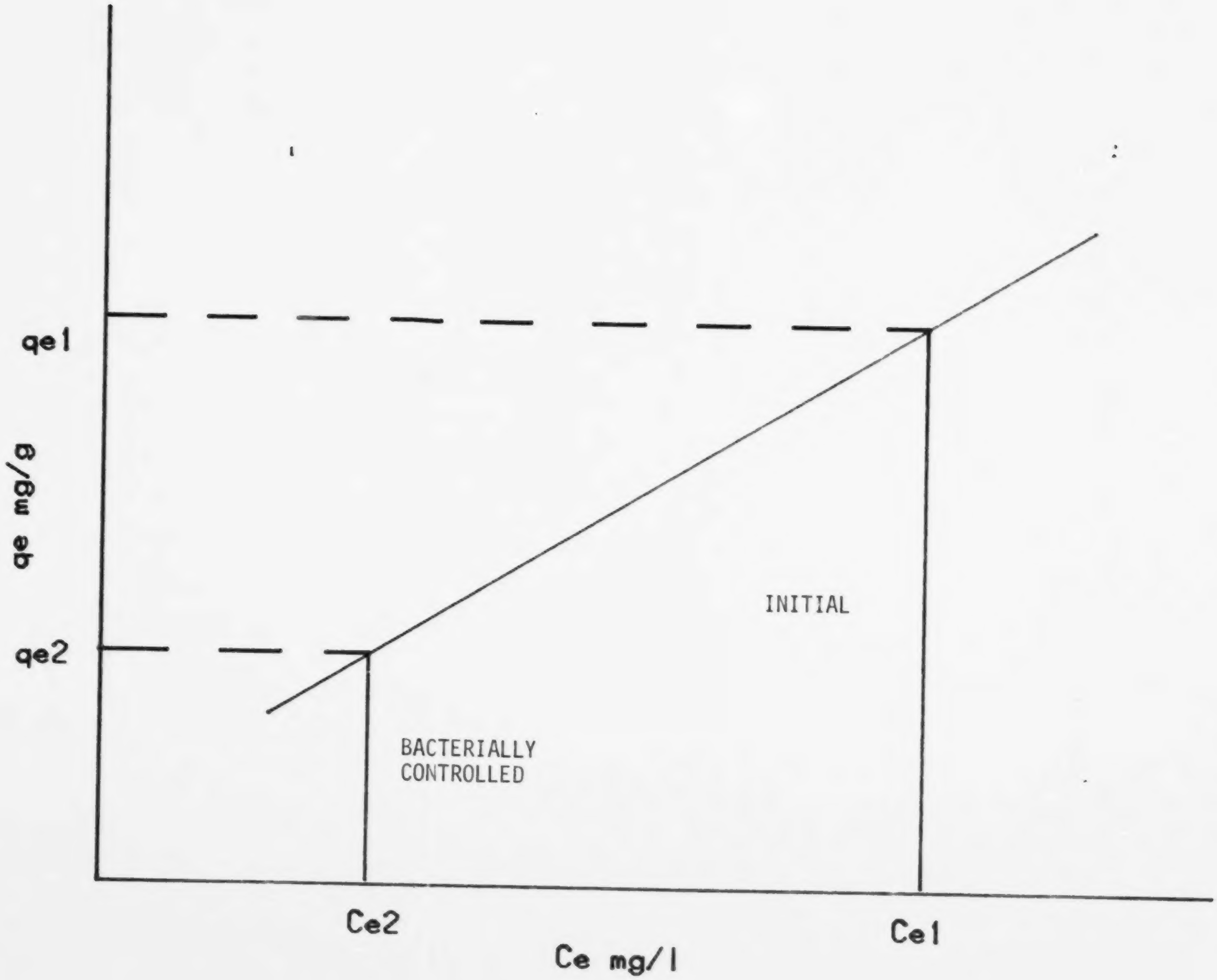

Figure 187. Bacterial Utilization of Substrate at Initial Colonization.

since a net loss of bacteria was observed across the GAC contactors although microbial populations on the GAC remained constant. Heterotrophic microorganisms have been shown to expend approximately 40% of substrate energy during growth and incorporate 60% into cell structure (189). Theoretically, if at this pseudosteady state, organic material produced by death of influent cells were the major source of nutrient material, then the net bacterial production,, measured as effluent bacterial densities should be approximately 60% of the influent bacterial concentration assuming all material from dead cells was utilizable. If we assume that some portion of the dead cells are non-utilizable (or adsorbed on GAC) then an effluent bacterial density of 50% of the influent bacterial density, as observed in this study, may not be a function of soluble or adsorbed substrate utilization. Data suggest that maintenance of large GAC bacterial populations at steady state may be the result of autolysis and the adsorption of bacteria by GAC rather than by utilization of adsorbed or dissolved organic material.

Comparison of bacterial production and TOC removal may suggest that they are closely related in that both production and removal were fairly constant during the study. Neither bacterial production nor TOC removal increased with the increasing influent TOC concentration during the study. This suggests that bacterial removal was growth limited because increasing the substrate (TOC) did not increase bacterial production. However, other data in the study suggest very strongly that the bacteria were living in a severely nutrient limited enviroment, e.g. a doubling time of approximately 6 days. If the environment were nutrient limited, then an increase in TOC should result in an increase in bacterial production and TOC removal. This was not observed, again suggesting that large bacterial populations on GAC are not directly related to removal of organic matter.

At steady state, if effluent bacterial densities (2-5 x 10^4 cfu/ml) are considered to be net production, when compared to growth yield data (185, 186), this production is equivalent to minimal substrate utilization (approx. 10 µgC/l) irrespective of source (ie., autolysis, in solution, or adsorbed).

Calculation of growth rates for bacterial populations in the 40 inch contactors (location 25,26) during pseudosteady state was carried out. While showing considerable fluctuation the population doubling times for columns 25 and 26 were 7.0 and 22 days respectively. No net loss of bacteria was found in either of these columns.

Theoretical Considerations -- The calculated substrate requirements measured as TOC for the measured bacterial production were found to be insignificant compared with total loss across the GAC columns. Moreover when compared to the TOC removal across sand columns (TOC Removal Rate Study), this loss accounted for less than 10% total removal. It is apparent that significant concentrations of biodegradable material then are obviously removed as a result of maintenance requirements of the contactor microbial populations. Previous attempts to relate TOC removal to effluent bacterial densities and to GAC bacterial density have been unsucessful.

While the results of the TOC Removal Rate comparison experiments indicate no enhanced biodegradation on GAC, effluent bacterial densities of the sand columns were generally found to be higher than those from GAC columns. Indications are that effluent bacterial concentrations are therefore not indicative of biological TOC removal. As a precursor to an explanation of this phenomenon it should be noted that investigators generally find higher bacterial denisities on GAC than sand (119, 127) (presumably as a result of surface area differences).

Identical TOC removal for parallel GAC and Sand columns with different effluent bacterial concentrations may be explained if these columns are considered to be partially closed continuous culture systems (190) in which the cell concentration in the column is greater than that in the effluent. The deviation from an "open system" can be described by the "closure index" (c):

$$c = 100 \left(\frac{1 - x_b}{x}\right)$$

in which x is the vessel bacterial concentration and x_b the effluent bacterial concentration. In this system heterogenous or plug concentrations of cells can be maintained which increase the rate of substrate conversion. For similar TOC removal across GAC and Sand, with higher effluent bacterial densities in the sand contactor effluent, this equation would predict lower bacterial densities attached to the sand, with less TOC being used for maintenance, and more for cell production. From the above equation it is therefore possible to determine cell production if one knows the average effluent and GAC cell densities. In a chemostat since biomass production is a function of limiting nutrient, if an average growth yield (cells/gC) is known it is possible to determine biological TOC removal. Van der Kooij (185, 191, 192) has reported yield factors for several species of bacteria which are organisms commonly isolated from GAC contactors. For concentration ranges of 25 ug/l to 1.0 mg/L Glucose carbon, average yield factors for a *Flavobacterium* sp., two *Pseudomonas* sp. and *Aeromonas hydrophilia* were 4.7, 5.0 and 3.8×10^3 c.f.u./ml/gC/L respectively. In our laboratory we have conducted experiments using an isolate of *Pseudomonas aerugionosa* from the Torresdale water treatment facility to determine a growth yield factor by the method of Van der Kooij (185). An average value determined was 4.05 x 10 cells/ml/gC/L. Using this value and the "closure index", biological TOC removal can be determined. Unfortunately insufficient data is available for calculations on all the columns studied. However column bacterial densities were measured on GAC columns (Location 25 and 26). A parallel Sand column to GAC column (Location 26) was run, across which bacterial TOC removal was measured. By substitution of the respective minicolumn bacterial densities, effluent densities and the yield factor into the following equation, the average calculated bacterial TOC removal for columns 25 and 26 was 240 and 560 mg C/L respectively.

$$\text{carbon used } (\mu g/L) = \frac{1}{\text{Closure Index}} \times \frac{\text{Effluent cell/ml}}{\text{Yield factor}}$$

Results of the TOC removal rate studies previously described also indicate shifts in maintenance production ratios. Using the calibration factor determined previously the concentration for carbon required for new cell production for the warm and cold GAC contactors can be determined by division of effluent cell concentration by this factor. Effluent cell concentrations for the warm GAC and cold GAC (5/40/80-11/13/81) were 2.1×10^4 and 3.38×10^4 cfu/ml respectively. This represents 10.5 & 16.7 μgC/l used for production for warm GAC and cold GAC respectively. When compared to bacterial removal, bacterial production on the cold GAC & warm GAC accounts for 5% & 16.7% of total removal respectively. This compares favorably with the 8.5% and 16% removal attributed to the cold and warm sand contactors used in the TOC Rate Study.

MINI COLUMNS

Reproducibility

A measure of reproducibility both within the study and between this study and others is necessary to judge the results of this study with respect to other GAC investigations. Cross comparison of dissolved oxygen demand, microbial population development and TOC removal with other studies is difficult because of variability of the organics in the influent waters, pretreatment processes, carbon types, and contact times. The study reported on herein will be discussed first.

Reproducibility within this study has been demonstrated for the parameters DO, TOC, A254, and bacterial density in the adsorption reproducibility experiment (see Figures 147, 148, 150 and 153). Further discussion of the parameter of interest, TOC, shows that the mass of TOC removed by a specific contactor was very well reproduced. The mass removed by a contactor is defined as follows:

$$\text{Mass Removed} = \frac{(Ci - Ce)_{j+1} + (Ci - Ce)_j}{2} \times (t_{j+1} - t_j) \times Q$$

where Ce = effluent TOC concentration, mg/l
Ci = influent TOC concentration, mg/l
t = time, days
Q = flowrate, l/day

Figure 188 shows the mass loading to the warm and cold contactor up to day 236. The mass loading would amplify effects of a small but consistent differential between the contactors. The small differences observed indicate that the average removals by these contactors are very reproducible. This shows that adsorption is not a function of temperature in the flow through system used here, in agreement with Weber (129).

Although the purpose of this study was to explore mechanisms in long term TOC removal, it must always be stressed that the purpose of a GAC application to potable water treatment would be to remove trace quantities of objectionable compounds of health and organoleptic concern, or their precursors. Reproducibility of the carbon adsorption process for trace compound removal is therefore of prime concern to interpretation of comparative treatment processes utilizing GAC. A parallel study of the trace

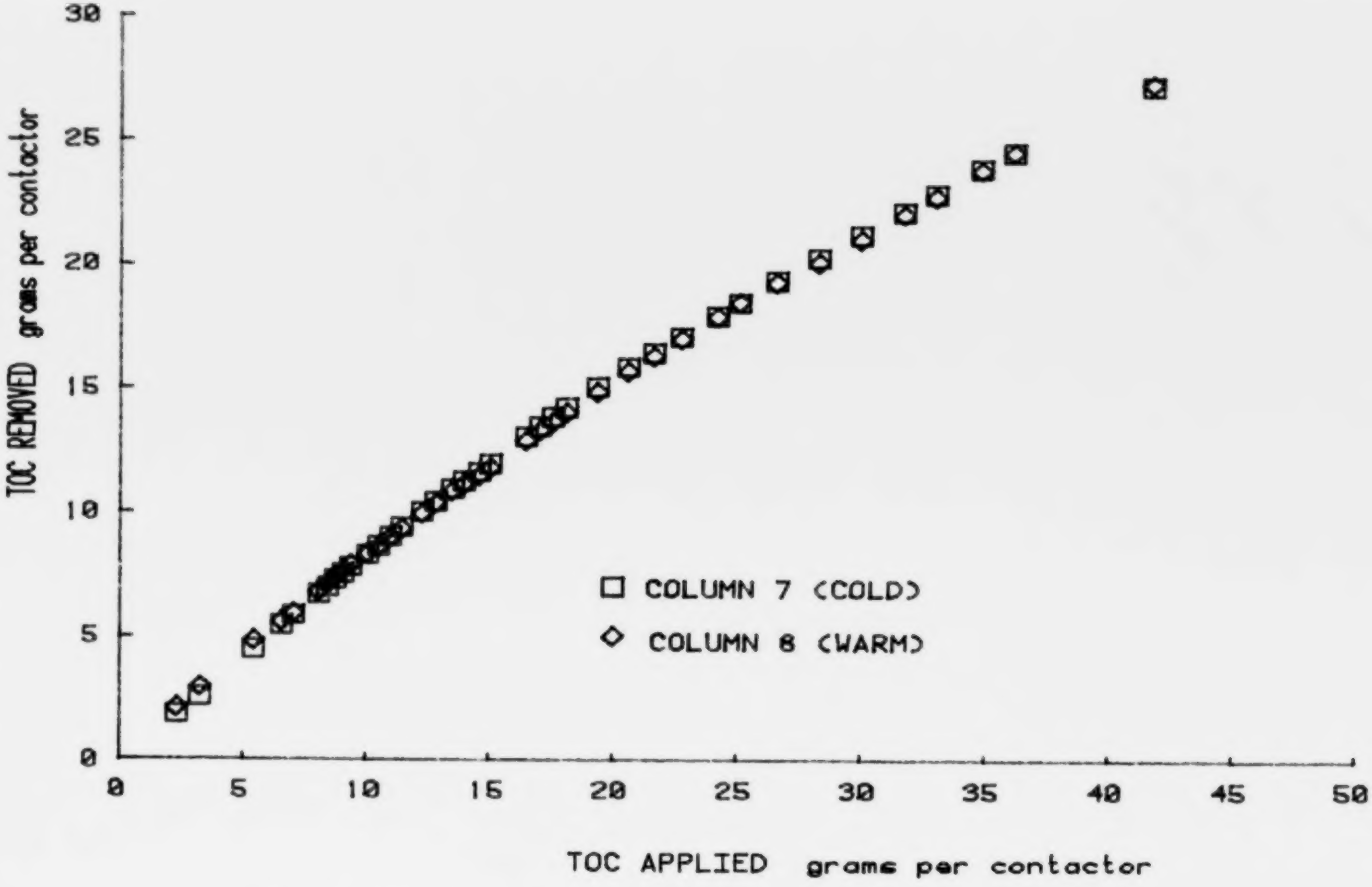

Figure 188. Mass loading of TOC for Column 7 (cold) and Column 8 (warm) Reproducibility Study - baseline for difference.

organic compounds was completed on the replicate carbon contactors and reported on elsewhere (See Appendix F). The reproducibility of the carbon contactors used in this study was demonstrated over a twelve week period for a broad spectrum of non-polar trace organics as collected on macroreticular resin accumulators and analyzed by the Chi-square statistic for chromatographic profiles.

In summary, reproducibility within the study reported on herein was demonstrated for dissolved oxygen demand, bacterial population development, TOC removal, A254 removal, and trace organic removal. Reproducibility was also demonstrated for pH and alkalinity, but the GAC adsorption unit process did not affect these parameters. The relationship between the results of this study and studies elsewhere in the world for the parameters dissolved oxygen demand, microbial population density, and TOC removal will be discussed in the following paragraphs.

Dissolved Oxygen

Typical dissolved oxygen demand data for the GAC adsorption unit process are presented for Bremen, West Germany (31) which show higher demands for summer months when temperatures were high. This data does not take into account differences in influent concentration, assuming that all oxygen demand is biological. Influent concentration (of oxygen) may effect the chemical removal of oxygen (unless the chemical reaction is zero order with respect to oxygen), but should not affect biological removal as long as the aqueous oxygen concentration is greater than 2 mg/l (193). Den Blanken (135) has also shown a temperature dependency of dissolved oxygen removal. The range of oxygen removal for Bremen is about 1 to 8 mg/l (31). The range of oxygen consumed for this study was <1mg/l to > 10 mg/l and therefore falls slightly out of the range at Bremen. However, the larger range in this study, particularly the higher values, were strongly affected by the artificial conditions of temperature control, therefore the dissolved oxygen demand in this study appears typical.

The effect of temperature on dissolved oxygen removal can be more reliably estimated from this study than others because the effect of a variable organic influent load is removed. The inverse relationship between oxygen solubility in water and temperature forces studies without temperature control to accept higher influent dissolved oxygen levels during seasons when bioactivity would be at a minimum due to low temperatures. This is irrelevant to studies involving bioactivity as the only mechanism for oxygen removal, because oxygen has been shown not to limit bioactivity at concentrations above 2 mg/l (193). However, high influent oxygen values could strongly affect a chemical reaction between oxygen and GAC, if oxygen enters into a concentration dependent chemical reaction with GAC. The existence of a chemical reaction between dissolved oxygen and GAC has been strongly suggested by Prober, et al (123) due to increases in surface oxides on GAC following reaction with dissolved oxygen. Reactions with other oxidants such as chlorine have also been shown to increase the surface oxides on GAC (195,29) and to form free carbon dioxide (196).

Thus the low oxygen removal values observed in this study, which occurred on the cold contactor during summer months when the influent dissolved oxygen concentrations were low, most probably result from effects on chemical removal of oxygen and do not indicate that this study is radically different from previous investigations. Similarly, high oxygen removals occurred when the warm contactor was receiving water supersaturated with oxygen (for the elevated temperature at which the warm contactor was operated), thus the higher rate of oxygen removal could result from high influent concentrations coupled with high temperatures, which could not occur in a "real" situation involving GAC treatment. This critical point of oxygen interaction with GAC and its implications in the use of dissolved oxygen demand in a carbon contactor will be discussed in a later section.

Microbial Populations

Microbial populations on the GAC and in the effluent water in this study agree very well with other investigators (113, 116, 119, 127). In general, the densities, in colony forming units (cfu), on the carbon was in the range of 10 million to 1 billion cfu/g with an average slightly below 100 million cfu/g, and the densities in the effluent water were 1 to 100 thousand cfu/ml with an average around 10 thousand cfu/ml. Therefore, results of microbial degradation in this study should agree with those of other investigators.

The effects and significance of the bacterial densities will be discussed in a separate section. The observed densities indicate that the GAC system at the Torresdale plant operated much the same as those elsewhere in the world. Therefore, the conclusions drawn from the data of this study in terms of bacterial activity and TOC degradation are drawn from a system operating similarly to systems elsewhere, which indicated enhanced rate of biodegradation on GAC (113).

TOC Breakthrough

Total organic carbon breakthrough characteristics have recently been reviewed by Roberts and Summers (133) for 13 investigations which were carried out in the United States and Europe. The general pattern of breakthrough is immediate breakthrough (generally less than 20%) of a small portion of the organics as measured by TOC, slow increase in effluent concentration to a relatively steady concentration which is less than the influent concentration. The ratio of effluent concentration (Ce) to influent concentration (Ci) for immediate breakthrough is usually in the range of 0.1 to 0.5 with most of the values falling below 0.2. The ratio of Ce/Ci at steady state lies in the range of 0.6 to 0.9, with a mean of 0.76. The EBCT for the thirteen studies ranged from less than 5 minutes to 35 minutes. There was considerable scatter in a plot of the ratio of Ce/Ci for initial breakthrough. The magnitude of initial Ce/Ci appears to decrease with increasing EBCT up to approximately 20 minutes.

The review included studies in which the influent concentration ranged from 1 to 16 mg/l. A dimensionless time parameter, the throughput ratio, was used to classify breakthrough as slow, median or rapid. This parameter is defined as:

$$\text{Throughput ratio} = \frac{V_t}{V_{GAC}}$$

where V_t = volume of water treated as of time t

V_{GAC} = bulk volume of GAC in the contactor

The point at which steady state was reached was defined as a Ce/Ci within 5% of the steady state value. Figure 189 shows a plot of the Ce/Ci for the warm contactor used in this study. Steady state occurs after about 300 days; therefore, the throughput ratio at steady state for this study is 32,000 bed volumes. Ce/Ci vs. throughput ratio is plotted in Figure 190. This type of curve was designated slow breakthrough by Roberts and Summers (133), but is within the range of the other investigations. The throughput ratio at steady state is also within the range of values reported.

In summary, the general characteristics of DO, bacterial density, and TOC removal observed in this study are typical of GAC applications throughout the world. The one exception is influent bacterial density. Most applications have suppressed the bacterial population through the use of disinfectants such as ozone or chlorine, so high influent bacterial densities observed in this study are not viewed as detrimental in the application of the conclusions of this study to other locations.

Dissolved Oxygen as a Measure of Bioactivity

Dissolved oxygen removal and rate of removal have been widely used in wastewater engineering as an indirect measure of bioactivity and rates of biological waste stabilization. Dissolved oxygen has also been applied as a measure of bioactivity in activated carbon contactors (22, 28, 122) although it is generally accepted that the initial high oxygen demands are chemical in nature (123).

The purpose of investigating dissolved oxygen as an indirect measure of bioactivity in GAC contactors was twofold. First, to judge the results of other studies which have used this parameter and second, to qualify the technique for use in comparative GAC systems.

Results from the oxygen uptake experiment indicate that a steady state oxygen removal occurs after approximately 200 hours for the operating parameters used in this study (see Table 12). These results were obtained using recycled distilled water which is assumed to have very low TOC. Based on this, and the fact that Prober, et al (123) found dissolved oxygen removal continuing up to 1700 hours with a concomitant increase in surface oxides, two removal phenomena are suggested in the interaction of oxygen and GAC; adsorption and chemical reaction. Adsorption was demonstrated by Prober, et al (123), when oxygen was recovered from GAC using anoxic water. Chemical reaction is indicated by the increase in surface oxides. Adsorptive capacity for dissolved oxygen appears to be rapidly exhausted whereas the chemical reaction may proceed indefinitely due to the high concentration of GAC relative to the dissolved oxygen. Reactions with other oxidants such as chlorine

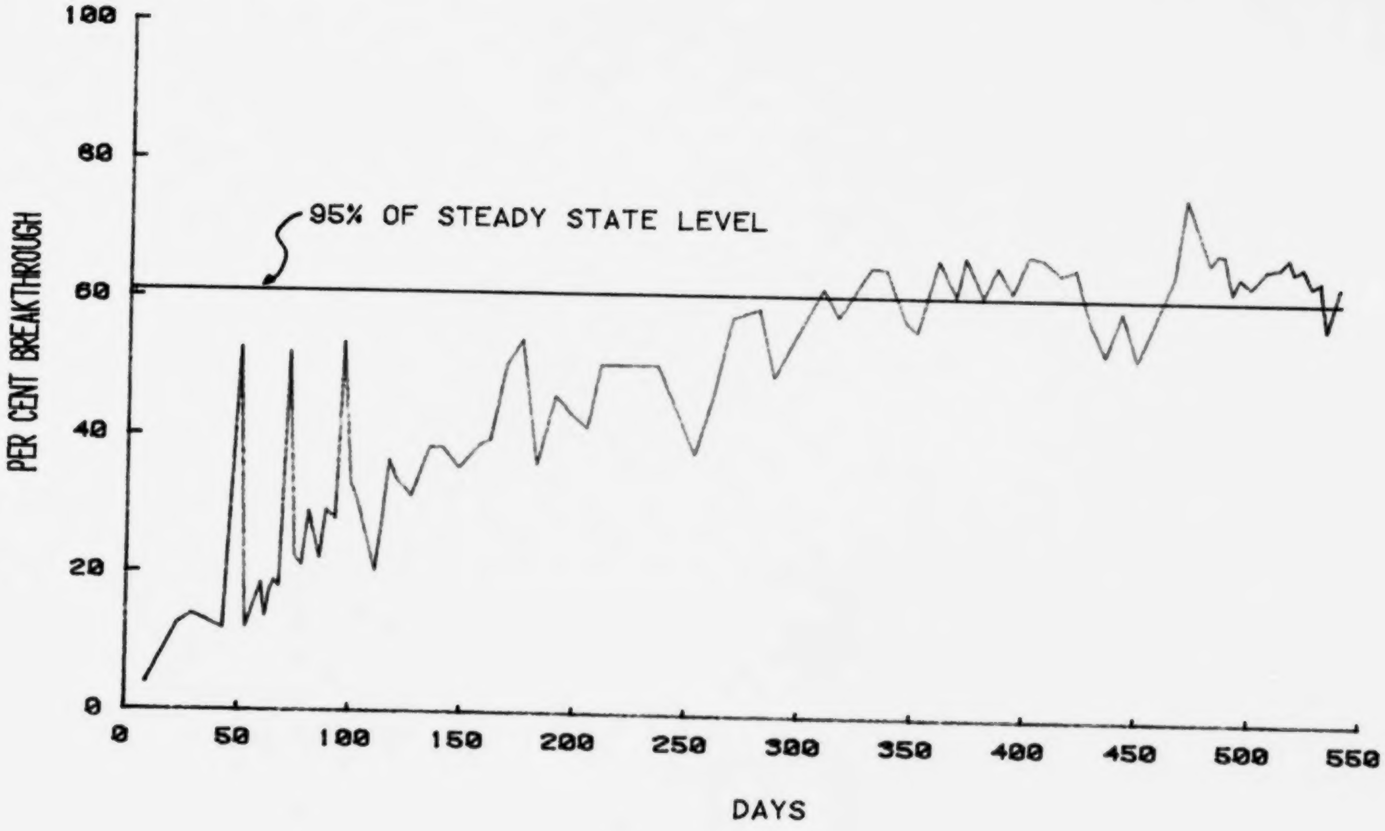

Figure 189. TOC breakthrough as a percent of influent for Column 8.

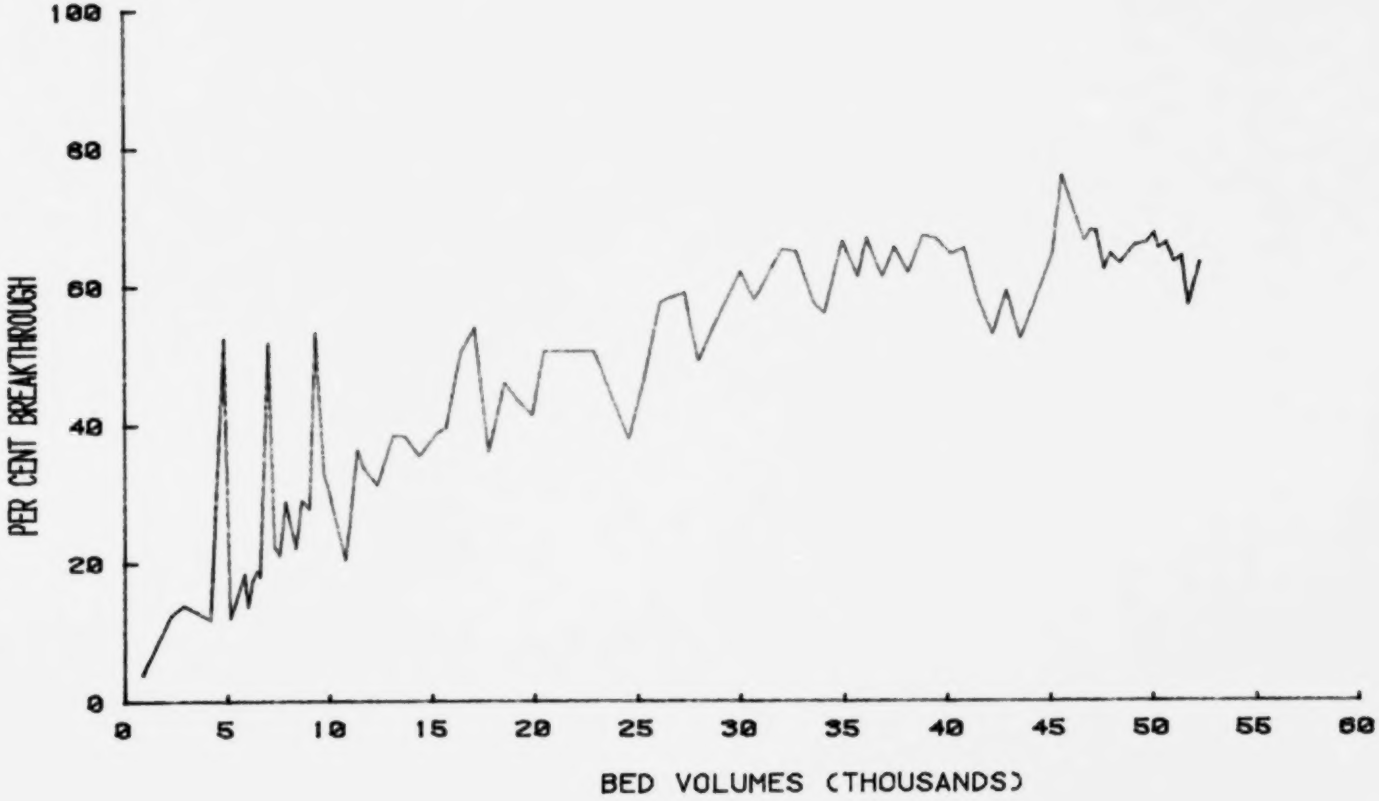

Figure 190. TOC breakthrough as a function of throughput ratio for Column 8.

have also been shown to increase the surface oxides on GAC (29, 195) and to form free carbon dioxide (196).

Oxygen is a milder oxidant than chlorine, and is not completely reduced on GAC as is the case for chlorine. However, the reactions of other oxidants suggest that oxygen may also react chemically with GAC. Prober's data supports the chemical reaction hypothesis, and the strong influence of temperature on dissolved oxygen removal on parallel GAC contactors operating at different temperatures (without an effect on TOC) also supports the hypothesis. Data (196) also exists suggesting that carbon dioxide may evolve from the carbon's surface upon reaction with an oxidant. This leaves the use of carbon dioxide evolution as a measure of bioactivity open to question in a contactor in which a chemical reaction between oxygen and GAC may occur.

Figures 155 and 156 show the dissolved oxygen and TOC profiles across the warm and cold carbon contactors. Note that at the onset of Mode B, when the influent to one of the contactors was initially chilled, the dissolved oxygen removal was immediately affected without a similar change for TOC removal. Figures 191 and 192 show the dissolved oxygen and TOC profiles, respectively, across the warm and cold carbon contactors for the entire study. The number of data points on these figures only enables one to interpret the general trend. The trend observed is an immediate effect on the dissolved oxygen without affecting TOC. This is particularly evident in Mode C (where the temperature on the warm contactor was increased suddenly from 15 to 30 degrees centigrade), when the greatest dissolved oxygen demand was observed without affecting TOC removal until after day 250, approximately 80 days after the onset on Mode C.

The data in this study suggest that the chemical oxygen demand exerted by GAC lasted throughout the study. The chemical reaction is suggested by the immediate effect of a temperature differential on dissolved oxygen removal which occurred every time the contactors were operating at different temperatures. It is important, therefore, to be able to estimate this chemical demand when using dissolved oxygen removal as an indirect measure of bioactivity. One such approach would be to assume zero order kinetics with respect to GAC (because of its abundance relative to oxygen) and use an equation of the following form:

$$d\,[O_2]/dt = ko\,\exp(-Ea/RT)\,[O_2]^n$$

This type of equation has been described previously in for TOC removal with the assumption that the reaction is first order with respect to TOC. In this equation n is the order of the reaction with respect to oxygen. The data in this study are unsuitable for estimating the variables ko, Ea, and n because biological and chemical dissolved oxygen removal were proceeding simultaneously. Based on the observations in this study and those by Maqsood and Benedek (44), it appears that bacterial activity can be masked by carbon until carbon's adsorptive capacity is at least partially exhausted. The GAC process gradually changes from purely a quick adsorptive TOC removal to a simultaneous slow adsorptive and biological TOC removal without a clear cut boundary. Furthermore, biological TOC removal with accompanying dissolved oxygen demand may occur on a GAC contactor even though its effects are not

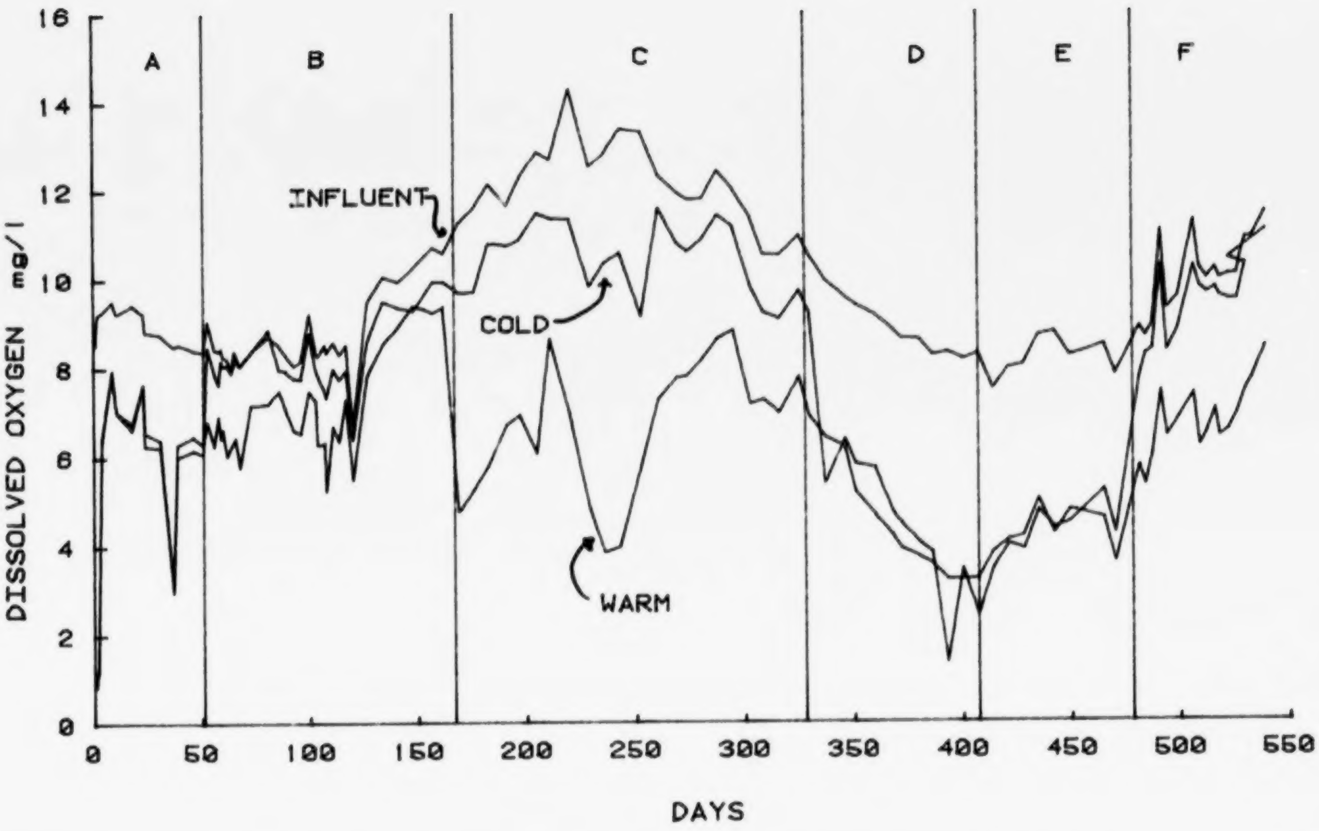

Figure 191. DO profile across GAC contactor for Column 7 (cold) and Column 8 (warm) - all modes.

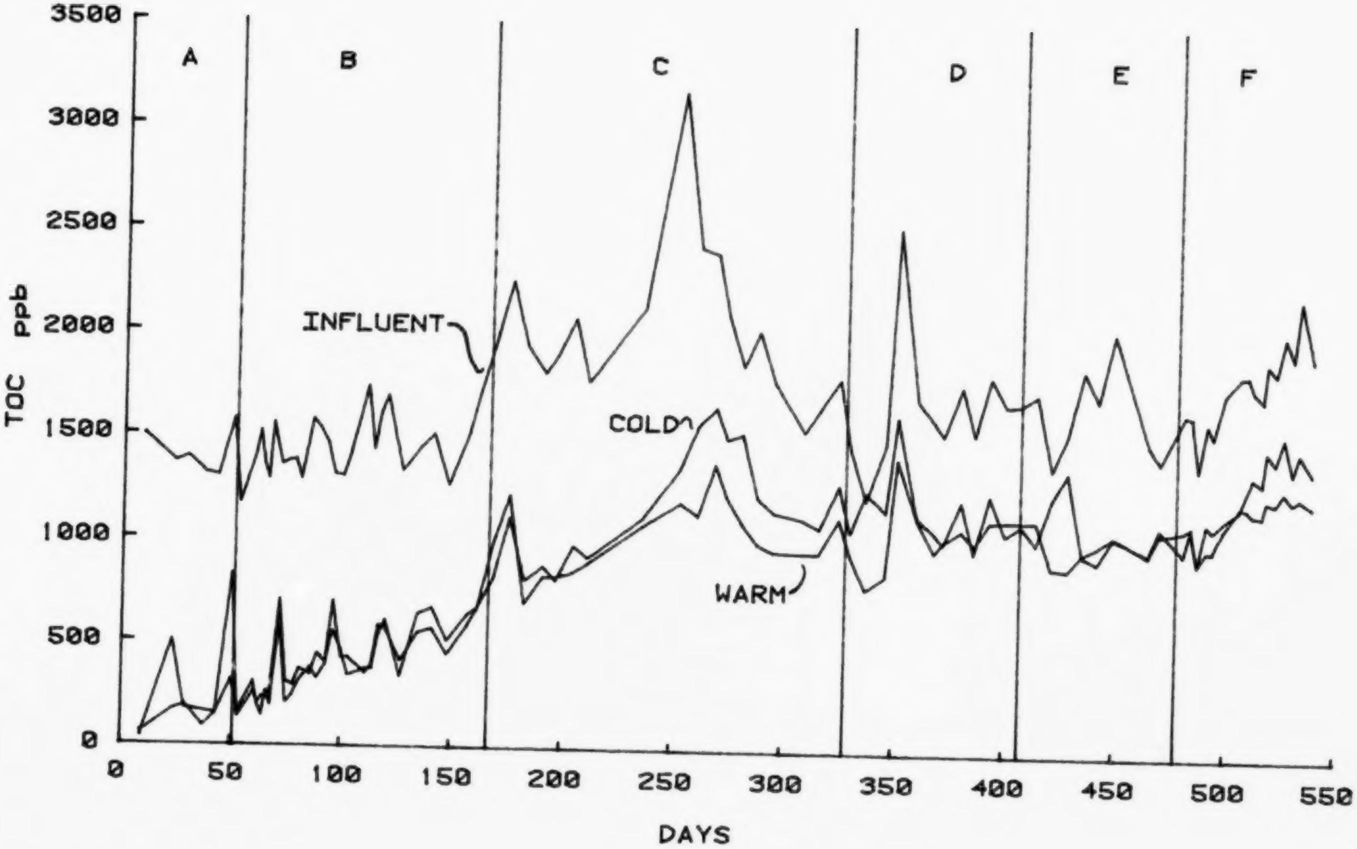

Figure 192. TOC profile across GAC contactor for Column 7 (cold) and Column 8 (warm) - all modes.

seen in the effluent. In other words, the influent end of a GAC contactor may become sufficiently exhausted with respect to TOC removal to allow biological activity to be important as a removal mechanism, but the effects of biological removal will not be seen in the effluent until the adsorption front has passed the effluent end of the contactor.

Figure 193 shows data supporting this proposed mechanism. Effluent dissolved oxygen values are plotted for three contactors; the cold contactor, the warm contactor and a control contactor which contained virgin carbon on day 124. In this figure, the control contactor is maintained at ambient temperatures and the dissolved oxygen concentration in the effluents of the warm and cold contactor are compared to the control contactor. Because this data spans a change in operational mode, the warm contactor is operating at ambient temperatures until day 167 and thus is compared to the control contactor only up to that day. After the change in operational mode, the cold contactor is at ambient temperature and thus is compared to the control contactor (which is also at ambient temperature).

Because of its short service time, the control contactor is assumed to be operating primarily as an adsorber. Up to the change in operational mode, there appears to be little difference in the dissolved oxygen removal between the older "warm" contactor and the control (virgin) contactor. After the change in operation, the older "cold" contactor consistently exhibits greater oxygen demand than the control contactor. Bioactivity is assumed to be responsible for the difference in effluent dissolved oxygen concentrations between the partially exhausted contactor and the control contactor. However, it was not until almost 100 days after the change in operational mode that a difference in TOC removal (assumed due to biological processes) was seen between the warm and cold contactors.

In summary, dissolved oxygen removal by activated carbon appears to have two components, one which is a chemical reaction with the carbon's surface and one which is mediated by the attached bacterial population. Dissolved oxygen removal can be used as an indirect measure of bioactivity if the chemical demand of the GAC is known, or estimated in parallel contactors. In the present study, no exact measure of chemical demand was determined.

Storage of Biodegradable Materials on Activated Carbon.

The comparison of a control and operating contactor illustrates a method for estimating increased bioactivity on GAC through the use of dissolved oxygen as long as an estimate of the chemical oxygen demand of GAC is made. A second aspect of the results of this experiment is the relationship of the high oxygen demand to the mode of contactor operation. The abrupt increase in oxygen demand suggests that the temperature change induced a shift in equilibrium, releasing adsorbed biodegradable materials to the aqueous phase.

Before the change in operation, no large temperature increases had been encountered. After the change, a temperature induced shift in adsorption equilibrium may have allowed previously adsorbed biodegradable organics to reenter the aqueous phase. Thus, the older contactor would have greater concentrations of biodegradable organics than the control contactor. This is

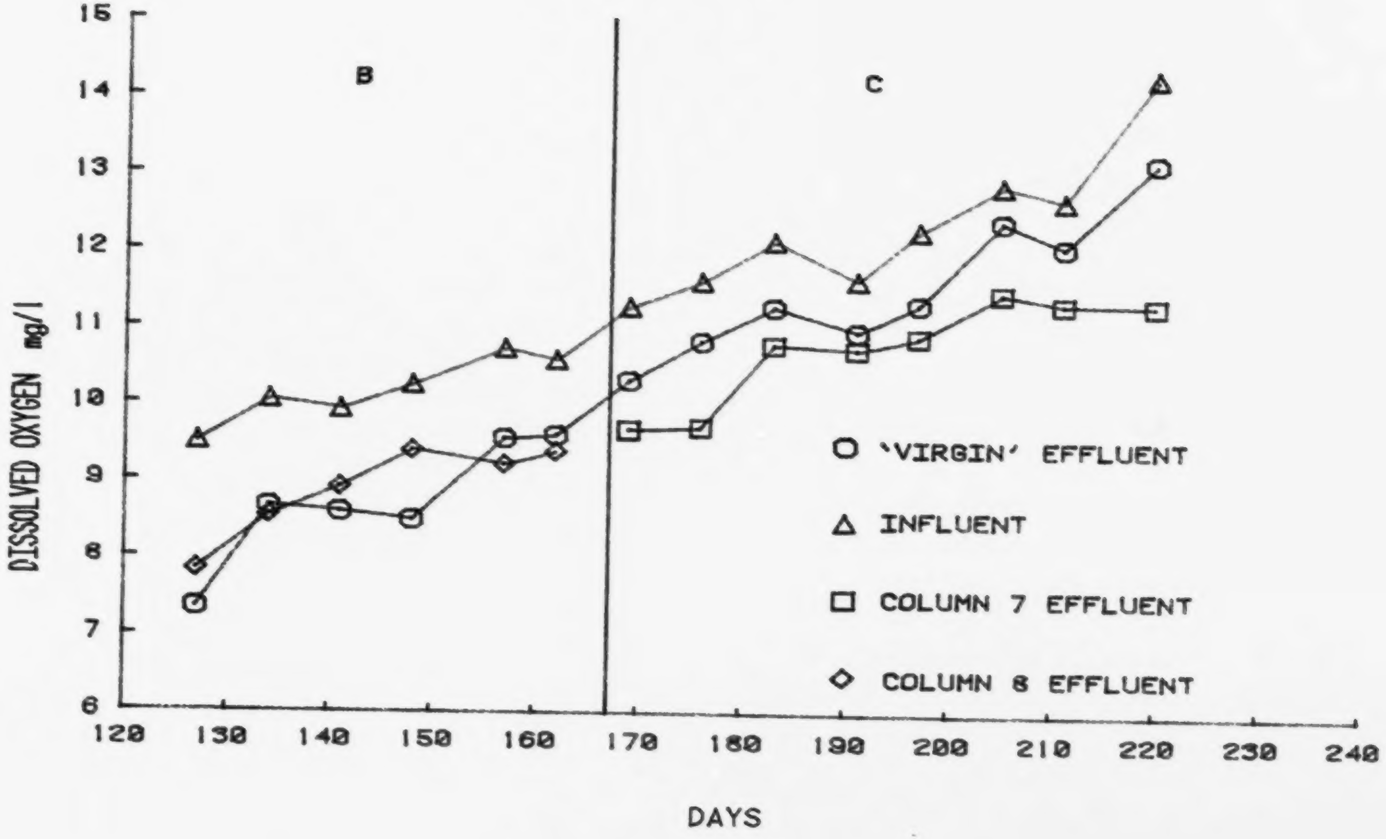

Figure 193. DO demand on GAC contactor - loaded vs. virgin carbon.

reflected in the dissolved oxygen demand, but not in the effluent TOC because the GAC's adsorptive capacity would mask the effects of the TOC that was not biodegraded. Thus, materials adsorbed at the top of the contactor could be desorbed and acted upon by bacteria, or adsorbed further down the contactor.

Results from sand contactors operated in parallel to the GAC contactors in this study give an estimate of the nature of biodegradable TOC in the contactors influent. Two sand contactors, each with 15 minutes EBCT, were operated in series receiving water from the ozone retention tank (see Figure 194). TOC removal was monitored across each contactor. All biodegradable material present in the ozone retention tank was removed in the first contactor. Figure 194 shows the TOC concentrations in the influent and effluents of the two sand contactors. The effluent from the first and second contactors (in series) are essentially the same. Thus, there should have been no excess biodegradable TOC to be released by a temperature induced shift in equilibrium, unless bacteria and GAC are competing for the organics. Furthermore, biological utilization of adsorbed substrate should have resulted in negligible storage, in that the sand system indicates that the biosystems were not taxed (in terms of insufficient hydraulic retention time) for TOC removal in the first sand contactor.

Figure 195 is another illustration that storage of biodegradable materials and a temperature induced shift in equilibrium were responsible for the high dissolved oxygen demand exhibited after the change in operational mode of the GAC contactors. Data for the warm contactor are presented for the warm contactor up to day 325. The first 167 days were at ambient temperature, and represent a temperature range that increases slightly in the early part of the study (from 20 to 29 degrees from June through August) and then continually declines to about 15 degrees centigrade when the operational mode was changed. These data (up to day 167) are plotted versus temperature as triangles on Figure 195 with the best fit line for the linear regression of dissolved oxygen removal against temperature. The 95% confidence interval for the regression is also plotted. The values represented by the diamonds represent the dissolved oxygen removals encountered after the change in operation. All of these values lie outside the confidence limits of the regression line. Although the correlation for the regression is poor ($r^2 = 0.24$), the fact that all the values after the change in operation lie outside the range indicates that some other mechanism is operating in the contactor after the change in operation.

In summary, dissolved oxygen removal by GAC appears to have biological and chemical components. It is a poor direct estimator of biological activity and requires a method for estimating the chemical oxygen demand of the carbon. Comparison of the control (virgin) contactor to the exhausted contactor appears to indicate that the GAC is able to store biodegradable materials. These materials can be acted on only if some environmental factor causes the adsorbate to desorb. The presence of adsorbed biodegradable material suggests that bacterial utilization of adsorbed substrate is insignificant, unless acclimization of bacteria to adsorbed substrate is an important mechanism.

The implication of insignificant biodegradation of adsorbed substrate

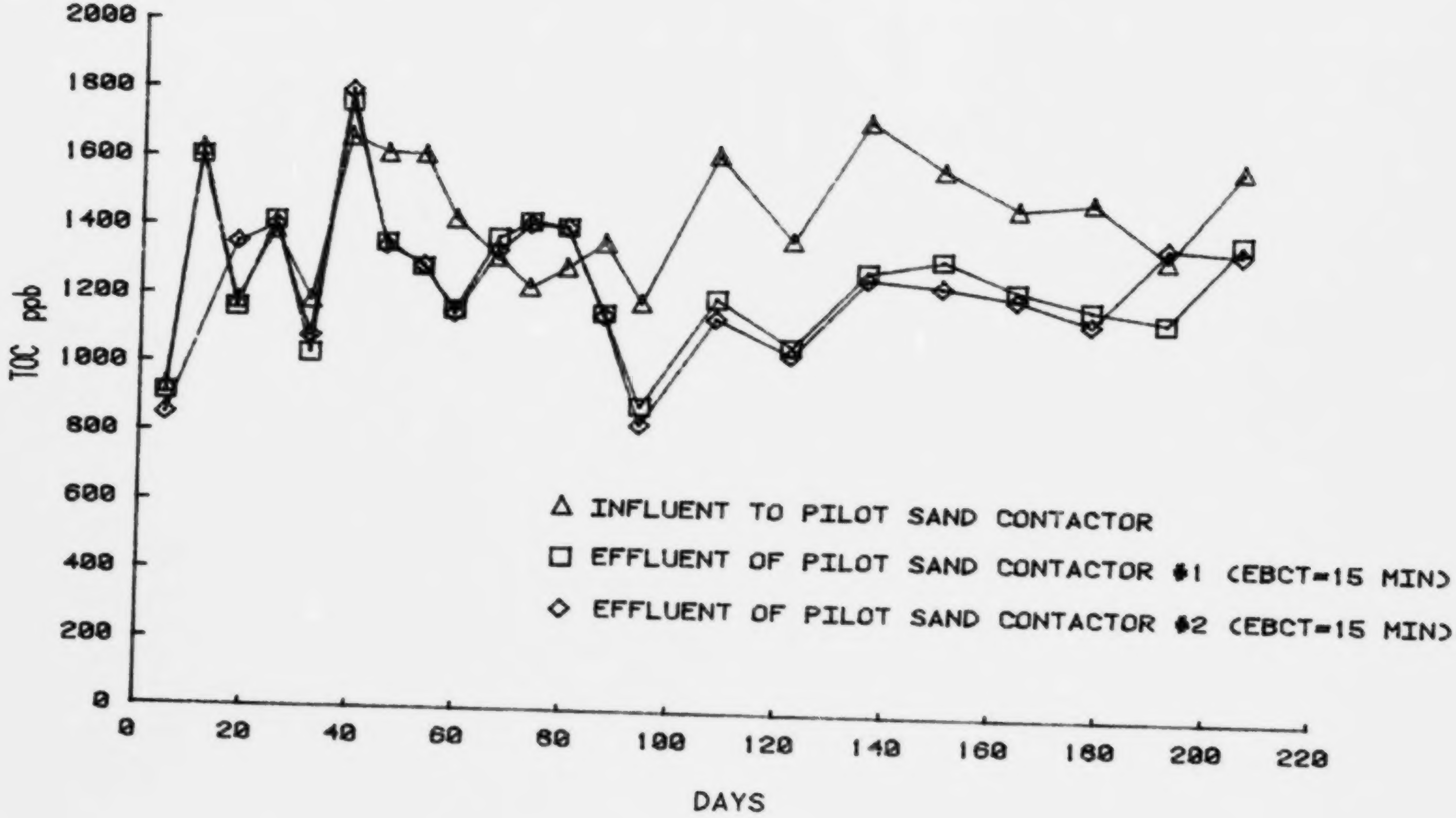

Figure 194. Pilot Plant sand contactor TOC profile for 15 and 30 minute EBCT.

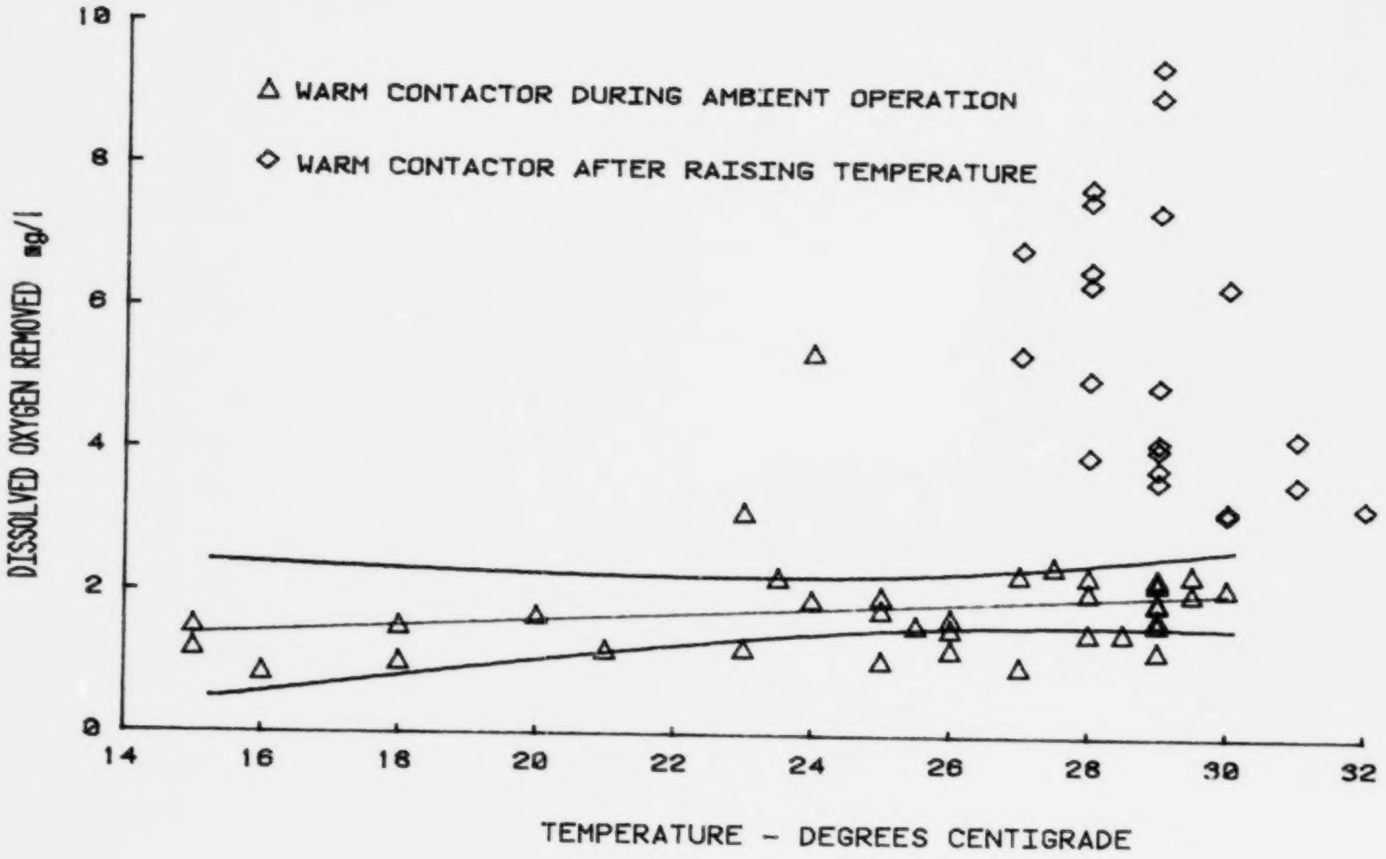

Figure 195. DO removal vs. temperature for Column 8 (warm) during Modes A, B, and C.

is very important to the theory of biological regeneration of GAC (112, 113). These authors emphasize that solutes must be adsorbed first, and then biodegraded. The data presented herein suggest that bacteria cannot use adsorbed substrate. This implies that biological regeneration is not an important mechanism. The only advantage GAC appears to have over an inert media is storage of biodegradable materials, which could result in GAC acting as a buffer to store materials when high concentrations of biodegradable, adsorbable compounds are present in the influent water. The importance of acclimization will be discussed in the following section.

Temperature Effects

The purpose of this section is to discuss how temperature effects adsorption and biodegradation in a GAC contactor and to interpret the results of temperature changes on a GAC contactor. Both observed results of the imposed temperature control used in this study and expected results of seasonal temperature changes will be discussed. The observed results will also be interpreted together with results from the TOC removal rate study to determine mechanisms for the temperature induced TOC removal differential.

The ability of temperature to control biological degradation of organic compounds (while having negligible effects on adsorption) was demonstrated during the long term study of the two GAC contactors which were operated both at differential and identical temperatures. During the first portion of the study, up to approximately day 240, the two GAC contactors exhibited nearly identical TOC removal. From day 50 to 240, the two contactors were operating at different temperatures (average differential = 15 degrees centigrade, see Table 13, modes B and C). From day 240 to approximately day 320, the warm contactor consistently exhibited greater TOC removal. Figure 155 shows that the warm contactor had a lower effluent TOC concentracion than the cold contactor. Based on these observations, at approximately 240 days into the study, it appears the ability of the adsorptive capacity of GAC to mask differential bacterial degradation rates (44) became exhausted.

Alternately, the difference in TOC removal can be explained on the basis of bioregeneration of the GAC surface on the warm contactor. Figure 156 shows that there is a marked increase in the dissolved oxygen removal (i.e., lower effluent dissolved oxygen) in the warm contactor compared to previous data for that contactor, some of which was collected while the contactor was experiencing the same temperature range as that at the onset of Mode C. This large removal diminished around day 250, or about the same time that the temperature induced TOC differential began.

The high dissolved oxygen demand compared to previous data suggests that there was a marked increase in biological oxygen demand. There was increased bioactivity on the cold contactor also, as evidenced by the data shown in Figure 193, but the increase in activity shown indirectly by dissolved oxygen demand was more pronounced on the warm contactor. Comparison to the control (virgin) contactor indicates that the increased oxygen demand was not due solely to changes in the influent concentration of biodegradable organics, otherwise there should be no difference between the cold exhausted and control contactor as shown in Figure 193.

Two explanations will be proposed for the observed phenomenon:

1. The higher temperature on the warm contactor accelerated biodegradation of adsorbed organics. This in effect cleansed the carbon's surface and provided more area for adsorption. This same phenomenon was occurring on the cold contactor, but at a lower rate. The carbon in the warm contactor was regenerated faster and thus had more renewed surface area. This greater amount of regenerated surface area was able to adsorb more organics than the regenerated surface area in the cold contactor, thus there was a differential removal of TOC. This explanation may be termed "temperature induced bioregeneration".

2. The sudden increase in temperature caused a shift in adsorption equilibrium for materials adsorbed on the GAC. As biodegradable material reentered the aqueous phase, bacteria mineralized it. This mechanism was discussed in the previous section and implies that bacteria cannot use adsorbed substrate. The mechanism of acclimization will be addressed in this section.

The temperature induced bioregeneration should occur in several steps. Consider first the source of the stored biodegradable organics on the warm contactor.Referring back to Figure 194, it appears that all readily biodegradable organics in the ozone retention tank can be mineralized in one sand contactor of 15 minute EBCT. The EBCT of the GAC contactor was also 15 minutes, therefore there should be no stored organics for biodegradation. However, one of the proposed mechanisms of enhanced biodegradation (27) on GAC is acclimization of bacteria to adsorbed organics. Therefore, the existence of the stored biodegradable organics may be attributed to acclimization of bacteria to adsorbed substrate.

The increased dissolved oxygen demand on the warm GAC could then be assumed to occur through the increased bacterial degradation of both adsorbed and aqueous organic carbon due to increased temperatures. This mechanism would occur on both warm and cold GAC, but would be more pronounced on the warm contactor because the change in temperature on the warm GAC contactor (from 14 to 30 degrees centigrade) was greater than on the cold contactor (from 6 to 14 degrees centigrade). The bioregeneration would be more rapid on the warm contactor, therefore more capacity would be regenerated on the warm contactor than on the cold contactor. The observed TOC removal differential could be analogous to comparing two contactors which had been on line different lengths of time. The newer GAC would be expected to show lower effluent TOC values, and would be analogous to the warm contactor, because the warm contactor had been more completely regenerated than the cold contactor due to the temperature induced faster rate of bioregeneration.

A test was devised to determine if regeneration of the carbon's surface was the underlying mechanism of the TOC differential. By day 325, the large demand for dissolved oxygen on the warm contactor had subsided, but the cold contactor was operating in temperature ranges similar to or lower than the range which had led to the hypothesized storage of biodegradable materials on the warm GAC contactor. Recalling that the TOC removal differential was attributed to more rapid bioregeneration on the warm contactor, and that, as of day 325, the TOC differential was still evident, it was hypothesized that the high dissolved oxygen demand could be duplicated on the cold contactor by raising it's temperature.

The presence of stored biodegradable organics on the cold contactor is evidenced by the TOC removal differential, which indicates that the surface of the cold contactor is more exhausted than the warm contactor. This explanation does not require differences in the rate of biodegradation to be significant or insignificant in the TOC removal rate differential, because the proof of bioregeneration would be a reoccurrence of the high dissolved oxygen demand on the cold contactor once its temperature had been elevated.

An experiment was designed to attempt to duplicate the conditions which had led to the high dissolved oxygen demand on the warm contactor, which occurred at the change from Mode B to Mode C (day 167). The former cold contactor was raised to the temperature of the warm contactor. This was carried out in Mode D, in which both contactors were operated in the range of 30 to 35 degrees centigrade. Referring to Figure 157, it can be seen that dissolved oxygen demand did not increase dramatically on the former cold contactor as it had on the warm contactor, and in fact the demand was much the same as observed on the warm contactor. Figure 158 shows that a consistent TOC differential was not obtained and that, at the onset of Mode D, the former cold contactor actually had greater effluent TOC concentrations. The TOC data for the two contactors became less similar, with the former cold contactor showing much more variability than the warm contactor.

This data is inconsistent with the hypothesized bioregeneration of the surface. This experiment, which was carried out in Modes D and E, did not confirm the theory of bioregeneration, but it is insufficient to refute the theory entirely due to:

1) the difference in service time at which the temperature was raised on the contactors

2) the phenomenon of displacement of weakly adsorbing materials by more strongly adsorbing materials

One compound does not actually displace another, but this is the result of the dynamic nature of the adsorption process.

Solutes are in a state of constant exchange between the surface and aqueous phase. As the concentration at the surface increases towards the equilibrium concentration, a molecule that gains enough energy to leave the surface phase is less likely to find a space in the same location of the contactor to which to readsorb, thus the molecule will spend more time in the aqueous phase. In this manner, the molecule may move down the contactor as the more strongly adsorbing molecules "displace" the weaker adsorbers. If the molecule is both adsorbable and biodegradable, it may be converted biologically while in the aqueous phase, and not return to the surface phase. In this respect, the concentration of biodegradable materials at the surface will decrease with time as a proportion of the total adsorbed organic material, because nonbiodegradable materials may remain in the contactor long enough to readsorb further down the contactor while the biodegradable organics would be mineralized.

The source of biodegradable materials in the second explanation would be the readily biodegradable materials present in the ozone retention tank. In the second explanation, bacteria are unable to use adsorbed organics and in fact are competing with the carbon's adsorptive properties for organic substrate, indicating that acclimization would not be an important mechanism. When the temperature was increased, a change in adsorption equilibrium is hypothesized to have released previously adsorbed organics to the aqueous phase where they were biodegraded. This caused the high dissolved oxygen demand, but did not occur on the cold contactor when its temperature was raised because the concentration of biodegradable organics at the surface of the GAC had been reduced due to the displacement phenomenon.

Comparing the data in this study to the review by Roberts and Summers (133) indicates that steady state organic removal as measured by TOC began about 300 days into the study. Therefore, the stored organics assumed responsible for the high dissolved oxygen demand at the onset of Mode C (day 167 to day 250) would have been adsorbed prior to reaching steady state, when the carbon contactor is assumed to be operating primarily as an adsorber. The temperature increase on the former cold contactor (Mode D, day 325) occurred after steady state had been reached. The lag between imposing the elevated temperature on the former cold contactor may have allowed the continual exchange process involved in dynamic equilibrium to reduce the adsorbed biodegradable materials to a minimal level. Thus, the effect of a shift in equilibrium would not be seen in the dissolved oxygen demand.

A last experiment was designed to see if a return to the ambient-chilled mode of operation would reinstate the temperature induced TOC differential. This was accomplished in Mode F, in which the TOC differential returned. It was also noted that the temperature of the cold contactor is more crucial than the magnitude of the differential. The large number of bacteria available to degrade the substrate once it diffuses to the proximity of the surface require severe temperatures (i.e., less than 7 degrees centigrade) to curtail their respiration enough to induce a TOC differential.

Based on the observations that 1) the large dissolved oxygen demand could not be duplicated on the "cold" contactor by raising its' temperature and 2) the TOC differential could be reinstated by returning to an ambient-chilled mode of operation, it is concluded that exhausting the carbon's adsorptive capacity is the principal mechanism behind the delay in a temperature induced TOC differential and that acclimization to adsorbed substrate is not a significant mechanism. Furthermore, it appears that low temperature will adversely affect the long term TOC removal exhibited by GAC in drinking water treatment, just as it did for wastewater (44). However, the adverse effects will be delayed by the capacity of the carbon to adsorb organic solutes. This implies that TOC removal efficiencies would be reduced in areas experiencing cold winters and that parameters that have been correlated with TOC, such as trihalomethane formation potential, may also show decreases in removal efficiencies during cold seasons.

Sand as Medium for Estimating Bioactivity of GAC

The purpose of the TOC removal rate study described earlier was to determine if, in fact, the rate of bioremoval of TOC is greater on GAC than it is on sand.

Sand has been used in this study as an inert media control in which the effects of adsorption (rapid or slow) and biological TOC removal can be separated. Thus, biological removal will be that which occurs on sand, and adsorptive removal will be the difference between GAC removal and sand removal. There are serious questions in the literature regarding the use of sand in this manner due to greater long term TOC removal on GAC than on sand (113) and greater bacterial densities on GAC than on sand (119, 127). Although the rate of biological TOC removal cannot be measured directly on GAC, it has been demonstrated in this study that temperature can control bioactivity to a detectable degree while not affecting adsorption (i.e., during the early part of the study, while GAC was acting primarily as an adsorber, the mass loading curves were nearly identical). Therefore, comparison of the effects of temperature control on the TOC removal rates on sand and GAC can be used to measure differences in TOC removal rates by bacteria. If the temperature induced differential is greater on GAC than it is on sand, the overall biological rate is greater on GAC than on sand.

Figure 163 shows the effluent TOC values for the four contactors used in the TOC removal rate experiment. Table 86 gives the removals on the four contactors. Note that GAC consistently removes more TOC than sand, but the difference in the average removal over the study period between warm GAC and cold GAC is approximately the same. Figure 196 shows the cumulative mass removed by the four contactors. The differential mass removed between warm and cold GAC (758 mg) was nearly identical to that on sand (746 mg).

The four mass loading curves in Figure 196 were analyzed for statistically significant differences. The data were fit to a steady-state equation for TOC removal as a function of influent organic concentration (TOC), as follows:

$$\text{Mass Removed} = (\%\ \text{Removal}) \times (\text{Mass Applied})$$

This equation is the definition of steady state removal. The theoretical mechanism of linear proportionality between substrate applied and substrate removed biologically will be discussed in the following section. The mechanism of linear proportionality between TOC applied and TOC removed for adsorptive processes has been developed by Peel and Benedek (32). The adsorptive removal is not linear overall, but when viewed for a short period (after the initial rapid adsorptive breakthrough) it appears linear. In terms of long term TOC removal, two months (the duration of the TOC Removal Rate experiment) is a short time.

Tables 87 and 88 compare the regression lines for the mass loading curves generated from the warm vs. cold GAC and the warm vs. cold sand, respectively. The correlation coefficients are all greater than 0.99, therefore there is a strong linear relationship between mass applied and mass removed for all mass loading curves shown in Figure 196. Tables 87 and 88

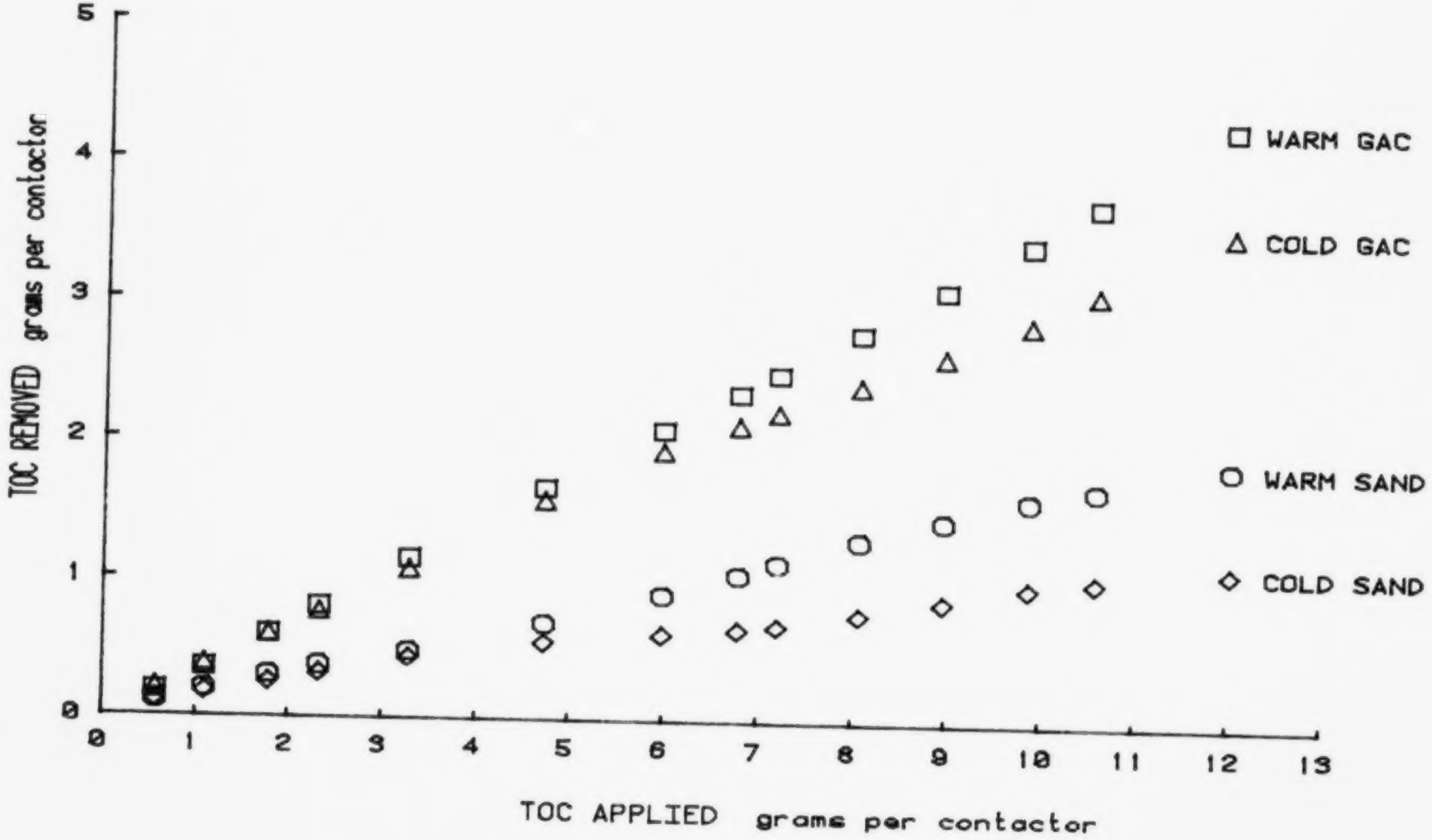

Figure 196. Mass loading curves for GAC and sand contactors on Columns 7, 8, 11, and 15 - TOC removal rate study, Mode F.

TABLE 86. REMOVAL OF TOC BY GAC AND SAND
EBCT = 15 MINUTES, ALL VALUES PPB (1)

DAY	WARM GAC	COLD GAC	WARM SAND	COLD SAND
1	555	674	402	451
4	525	537	283	228
7	446	453	189	128
11	648	480	257	189
14	546	451	153	183
19	648	609	211	220
26	629	639	301	69
32	569	413	309	119
36	559	405	348	64
38	659	423	404	181
42	624	430	311	190
46	746	485	321	221
50	689	552	348	252
53	952	737	116	30
59	703	547	379	205
MEAN	632	522	289	182
STANDARD DEVIATION	117	103	88	100

(1) Standard Deviation of Analytical Technique = 100 ppb

also compare the curves for differences between warm and cold contactors using GAC or sand as a media. The analysis indicates that the temperature induced TOC removal is significantly different ($p<0.005$) on both sand and GAC.

To test the theory that the bioremovals on sand and GAC were equivalent, the differential masses removed between the warm and cold GAC were compared to the differential removals between warm and cold sand contactors. It is hypothesized that the biological removal is as described in the Description of Studies section, and that the two reaction rates, kw and kc, for

TABLE 87. STATISTICAL ANALYSIS: WARM VS. COLD GAC MASS LOADING CURVE

Parameter	Regression 1	Regression 2
Slope	0.3526	0.2848
Intercept	-0.0298	0.1151
Corr. Coeff.	1.000	0.998

H_o: Slopes are Equal
t-Statisitic for Slopes = 13.139
Degrees of Freedom for Slopes = 24
Critical Value = 3.091. Therefore Reject H_o

TABLE 88. STATISTICAL ANALYSIS: WARM VS. COLD SAND MASS LOADING CURVES

Parameter	Regression 1	Regression 2
Slope	0.1567	0.0350
Intercept	0.0043	0.1037
Corr. Coeff.	0.998	0.996

H_o: Slopes are Equal
t-Statistic for Slopes = 21.103
Degrees of Freedom for Slopes = 24
Critical Value = 3.091. Therefore Reject H_o

the warm and cold contactor, respectively, are a function of temperature. Thus kw and kc would be related through the Arrhenius relation.

The rates kw and kc are assumed to be equal on both media, as is their difference, kw-kc. The equations being compared when analyzing the differential removals on GAC between warm and cold contactors (and similarly on sand) are of the following form:

$$dR = (kw-kc)[TOC]_A$$

where dR = differential mass removed
$[TOC]_A$ = TOC available for biodegradation

The analysis will determine whether TOC available for biodegradation is greater on GAC than on sand. The subtraction removes the effects of adsorption, as adsorptive TOC removal is unaffected by temperature. This has been demonstrated for the contactors in this study.

The differential mass loading curve generated from day 1 to 236 for the warm - cold GAC contactor (i.e. prior to any apparent trend in differential mass removal) will be used as a baseline to estimate the variability in the mass loading curve due to the summation of analytical, sampling and handling errors introduced in this method of analysis. In this manner, differences between the contactors removal mechanisms in two time frames, or two locations on the breakthrough curve, can be determined and a baseline of error will be established. The curves will be analyzed by linear regression (based on the assumption of first order TOC removal). The regression lines are analyzed in Tables 89, 90, and 91, for warm-cold sand vs. baseline, warm-cold GAC vs. baseline and warm-cold GAC vs. warm-cold sand, respectively.

Using the method of Zar (197), the lines were compared. The slopes of the warm-cold GAC and warm-cold sand regression lines were determined to be the same ($p<0.005$, see Table 91) and both were different from the baseline. The elevations (intercepts) of the warm-cold GAC and warm-cold sand were also determined to be statistically equal. Therefore, the lines coincide, and the effect of temperature on the rate of TOC removal is the same on GAC and sand. Based on this, it is concluded that biological TOC removal on sand and GAC is nearly equivalent, and that sand is a viable medium to compare biological and adsorptive TOC removal in GAC studies.

The statistical evaluation shows that at <0.01, the elevations are different.However, the slope is the most important criteria as it is a direct measure of the per cent removal (i.e. slope x 100 = per cent removal for linear mass loading curves).

Another point to be made in regard to estimating bioactivity on sand or GAC by temperature induced differential removal rates is the range of temperatures to be employed. The pilot plant data for TOC removal (see Figure 194) indicates very rapid removal of biodegradable TOC, i.e., all removal in 15 minutes EBCT. Referring to Figure 162, the differential removal between cold and warm contactors was not detectable on either the sand or GAC during the early part of the TOC removal rate experiment. This was

TABLE 89. STATISTICAL ANALYSIS: WARM-COLD SAND VS. BASELINE

Parameter	Regression 1	Regression 2
Slope	0.0716	0.0063
Intercept	-0.0994	-0.0771
Corr. Coeff.	0.983	0.436

H_o: Slopes are Equal
t-Statistic for Slopes = 7.323
Degrees of Freedom for Slopes = 48
Critical Value = 2.943. Therefore Reject H_o

TABLE 90. STATISTICAL ANALYSIS: WARM-COLD GAC VS. BASELINE

Parameter	Regression 1	Regression 2
Slope	0.0678	0.0063
Intercept	-0.1447	-0.0771
Corr. Coeff.	0.988	0.438

H_o: Slopes are Equal
t-Statistic for Slopes = 6.775
Degrees of Freedom for Slopes = 48
Critical Value = 2.943. Therefore Reject H_o

TABLE 91. STATISTICAL ANALYSIS: WARM-COLD GAC vs. WARM-COLD SAND

Parameter	Regression 1	Regression 2
Slope	0.0678	0.0716
Intercept	-0.1447	-0.0994
Corr. Coeff.	0.968	0.983

H_o: Slopes are Equal
t-Statistic for Slopes = 0.597
Degrees of Freedom for Slopes = 24
Accept H_o for Slopes, $p<.005$
Critical Value = 3.091
Common Regression Coefficient = 0.070

H_o: Elevations are Equal
t-Statistic for Elevations = 2.995
Degrees of Freedom for Elevation = 25
Accept H_o for Elevations, $p<.005$
Critical Value = 3.078
Therefore Lines Coincide

due to problems with the temperature control system. Once a steady cold temperature of 7 degrees centigrade or less was achieved, the TOC differentials and divergence of mass loading curves became detectable. The warm contactor operated between 16 and 19 degrees centigrade during the final portion of the TOC removal rate experiment. Thus, it appears that the low temperature is more important to control than the temperature range.

Comparison of the warm and cold contactors allows one to estimate the effects of temperature on the diffusion process in this study. Although diffusion is not expected to affect the adsorption process (128), it may affect the availability of substrate to the bacteria, because the bacteria are on the surface (carbon or sand). Thus, the substrate must move from the bulk liquid to the film surrounding the surface. This mass transfer applies to both the biodegradable and non-biodegradable chemical species.

The rate of diffusion depends not only on the rate constant for diffusion, but also the concentration gradient. Temperature would affect the rate constant, but the effect is expected to be minimal compared temperature effects on the biodegradation rate constant. Accelerated biodegradation (as proposed for GAC) would induce a greater concentration gradient by suppressing the organic concentration within the film. Thus, in the presence of accelerated biodegradation on GAC compared to sand, the temperature induced TOC removal differential should have been greater on the GAC than on the sand even if the differential were a result of altering the diffusion rates rather than the biodegradation rates. Thus the conclusion regarding biological TOC removal on sand and GAC remains the same whether film diffusion or biodegradation rates induced the TOC removal differential.

Theoretical Considerations

The proposed mechanisms in long term TOC removal would indicate that GAC should be a better medium than sand for bioremoval (due to the presence of higher bacterial densities). However, the finding that bioactivity is equivalent on sand and GAC is consistent with other microbiological literature. Using the Michaelis-Menten equation as a model of the kinetics of substrate removal, a rate expression based on bacterial densities and substrate concentration can be developed which indicates that there should be no enhanced bioactivity on GAC compared to sand. The purpose of the Michaelis Menten model is to help understand the process. Data to evaluate the specific kinetic constants were not determined in this study. The equation is as follows:

$$V_o = \frac{V_{max}\,[S]}{K_m + [S]}$$

where V_o = reaction rate
V_{max} = maximum reaction rate
K_m = Michaelis-Menten constant
$[S]$ = substrate concentration

In this expression, V_{max} is the reaction rate at which all bacteria are degrading substrate at their maximum rate. This equation can be derived for any reaction that exhibits saturation kinetics. In other words, there is a material which does not enter into the reaction which is required for the reaction to proceed (e.g., an enzyme system) which can become saturated with reactants and thus limit the reaction. Zobell (124), using bacterial densities less than 1 million/ml, demonstrated that bacterial substrate utilization was proportional to substrate concentration below 10 mg/l of substrate. This would indicate that saturation of an enzyme system does not occur when bacterial densities are greater than 1 million/ml and the organic concentration is below 10 mg/l.

More recently, Lawrence and McCarty (136) have measured growth constants for treated wastewater, finding a K_m of 22 mg/l as chemical oxygen demand (COD). This was discussed in the Description of Studies section. TOC in the river would most likely be less biodegradable than fresh effluent from a wastewater treatment plant. For these reasons, it appears likely that the bacterial populations on the GAC and sand were not near saturation with biodegradable TOC. Therefore, no advantage would be expected from higher bacterial densities on GAC compared to sand. This is analogous to forcing a chemical reaction to pseudo first order by providing all reactants except one in abundant quantities. The limiting reactant here would be biodegradable TOC.

Comparison of this study with Eberhardt's data (113) indicates that the rate of TOC removal observed on GAC in this study (range: 2 to 2.5 g/cubic meter/hour) was approximately the same as that of Eberhardt (range: 1 to 4 g/cubic meter/hour). The large difference between this study and Eberhardt lies in the sand data; the rate in this study being 0.66 to 1.1 g/cubic meter/hour, whereas Eberhardt reports a rate of 0.02 g/cubic meter/hour. The other difference is that this study used a relatively rapid sand filter while Eberhardt made comparisons with a slow sand filter. Based on the data from the two sand contactors in series, all bioremoval would occur in the first 15 minutes (or less) of contact. Increasing the contact time would not increase the removal, therefore increasing the contact time will only decrease the apparent efficiency of bioremoval. This may explain why Eberhardt determined such a low efficiency for the sand. It is not possible to determine the EBCT of the slow sand filter used by Eberhardt.

In summary, sand appears to be a viable medium for comparing biological TOC removal with that on GAC at the experimental conditions of this study. The rates of biodegradation were measured to be the same by comparing the temperature effects on the rates. This study does not imply that the rates on GAC and sand are always equivalent. This may be particularly true in wastewater treatment with activated carbon, where the concentration of biodegradable organics is much higher, and saturation of bacterial enzyme systems may occur. The method of temperature controlled TOC removal comparing GAC and sand shown in this section may be used to determine if the overall biological TOC removal on GAC is greater than that on sand in wastewater treatment. The theoretical possibilty of saturation of enzyme systems indicates that studies at high organic concentration should not be extrapolated to potable water treatment situations where the organic concentrations are low.

Bacterial and Adsorptive Contributions to TOC Removal

The verification of sand as a medium to estimate the TOC removal occurring biologically on GAC allows adsorptive TOC removal to be estimated by subtraction. Table 92 is an analysis of the mass loading data for differential removal between warm GAC and warm sand versus the differential removal between cold GAC and cold sand. The slopes are determined to be equal statistically up to $p<0.5$ (t statistic = 0.685 for 24 degrees of freedom), therefore, the removal attributed to adsorption is determined based on the common (or weighted) regression coefficient (see Table 92). The removal is approximately 20% of the TOC applied (i.e., 20% of influent).

The bacterial contribution is a function of temperature and can be determined from the regression coefficients of the warm and cold sand mass loading curves (see Table 88). The removals are approximately 16% and 8.5% for warm and cold sand, respectively.

Implications for GAC in Water Treatment

The purpose of this section is to discuss the results of this study with respect to the overall pilot plant study of which this research was a part and to review the use of ozone in water treatment. Five subtopics will be included as follows:

1) Implications of this study to methods used in the pilot plant study of GAC at Philadelphia.

2) The use of ozone prior to GAC in water treatment, commonly referred to as the "BAC" process (112)

3) The combined unit processes of ozone prior to sand as a method to reduce TOC in natural waters.

4) The combined unit processes of ozone, followed by sand, followed by GAC as a method to reduce both TOC and specific organics in water treatment.

5) The use of predictive models for design of carbon adsorption unit processes in water treatment.

Implications to Pilot Research in Philadelphia

The results of this research also indicate that the City was justified in using sand as a medium to estimate biodegradation in GAC contactors. The use of sand as a medium for estimating bioactivity on GAC was discussed in a previous section, and the results indicated that the rates of biodegradation were equivalent on GAC and sand.

The reproducibility of results obtained in this study provide a basis for comparison of the five treatment trains of the overall pilot plant. The results of this study demonstrated that identical parallel carbon contactors are reproducible for TOC removal, bacterial densities, dissolved oxygen

TABLE 92. STATISTICAL ANALYSIS: WARM GAC-WARM SAND VS. COLD GAC-COLD SAND

Parameter	Regression 1	Regression 2
Slope	0.1959	0.1997
Intercept	-0.0338	0.0114
Corr. Coeff.	0.997	0.996

H_o: Slopes are Equal
t-Statistical for Slopes = 0.584
Degrees of Freedom for Slopes = 24
Accept H_o for Slopes, $p<.005$
Critical Value = 3.091
Common Regression Coefficient = 0.198

H_o: Elevations are Equal
t-Statistical for Elevations = 2.932
Degrees of Freedom for Elevation = 25
Accept H_o for Elevations, $p<.005$
Critical Value = 3.078
Therefore Lines Coincide

demand, pH and alkalinity. In a concurrent evaluation for removal of specific organics as determined by broad spectrum analysis (See Appendix F) demonstrated reproducibility for the carbon contactors. Thus, a baseline for comparison of treatment trains which did not include replicates was established on the small scale columns.

Water Treatment by Use of Ozone/GAC

The combined unit processes of ozone followed by GAC adsorption (the so-called "BAC" process) was proposed to extend the useful life of a GAC contactor (31, 45, 56, 112, 113) by making it function as both an adsorber and support for biological processes simultaneously. These researchers attributed all organic carbon removal at steady state to biodegradation and proposed mechanisms (27) to explain the apparent faster rate of biodegradation on GAC compared to sand (113). These mechanisms were proposed prior to development of dual rate kinetic models (32, 33) which attribute long term TOC removal to adsorption hindered by slow diffusion into carbon's micropores.

The potential for implementation of the "BAC" process in the U.S. water industry received considerable attention including several pilot scale investigations of which Philadelphia's study was a part. Most studies did not address methods to separate biological and adsorptive TOC removal in the long term. The application of slow adsorption kinetic theory is not currently applied to pilot scale facilities, although most researchers do mention the theory in introductory statements. The results of this study indicate that the effects of biodegradation and slow adsorption can be separated at the pilot scale level and that slow adsorption in the micropores account for more than half of the TOC removal after as much as one and one half years on line.

The results also indicate that there is no enhanced biodegradation on GAC compared to sand, and that bioregeneration is not an important mechanism. Bioregeneration is very important to the "BAC" theory, because without it, the justification for the use of ozone lies only in the amount of TOC that can be removed in a sand contactor of equal EBCT. The observed storage of biodegradable TOC on GAC implies that bacteria cannot use adsorbed substrate, again showing that bioregeneration is insignificant, but also showing that GAC and bacteria are competing for dissolved organics in a contactor.

This observation is contrary to "BAC" theory, in that biodegradation may be slower (prior to steady state) on a GAC contactor than a sand contactor, because GAC withholds organics from the aqueous phase. Furthermore, if the biodegradable organics are unavailable to the bacteria when adsorbed, then they can be competing with nonbiodegradable and potentially objectionable organics. One of the principle justifications for removing TOC was competition with specific organics, however; if the TOC is not actually being biodegraded but rather adsorbed, there is no advantage to the "BAC" process.

Future studies should take the effects of slow adsorption into perspective, as ignoring this mechanism leads to erroneous conclusions about biodegradation on GAC. Long term TOC removal had been used as a justification of increased bioactivity on GAC, but once the effects of slow adsorption are determined, the long term removal on GAC is no greater than that on sand.

TOC Removal in Water Treatment by Ozone/Sand

Total organic carbon in raw water supplies is comprised primarily of humic materials (9). These materials are considered innocuous themselves, and therefore the removal of TOC is not a primary concern in water treatment, because it is not a good measure of specific organics. However, TOC may be a good measure of THM precursors (109) and has been shown to compete with specific organics (24) at natural background levels. Furthermore, it is relatively easy to determine compared to specific organics or broad spectrum analysis, thus it is attractive as a monitor of carbon contactor performance.

The mini column study has shown that biodegradation is equivalent on sand and GAC at steady state. The average removal for the sand contactors evaluated in this study were from 9% to 16% removal of mass applied. This was determined to be temperature sensitive, with the higher rate derived for contactors operated at 16 to 19 degrees centigrade and the lower rate determined for contactors operated at 5 to 11 degrees centigrade. Parallel studies on the pilot scale have shown that the rate can exceed 20% of the applied mass, but the average was 14% for one years operation in which the temperature of the contactor ranged from 2 to 30 degrees centigrade.

TOC Removal in Water Treatment by Ozone/Sand/GAC

The use of ozone and GAC for TOC removal may be best applied by inserting a sand bed between the ozone contactor and a GAC adsorber. This would allow the biodegradation to proceed prior to contact with GAC. The results of the study reported on herein indicate that bacteria may have to compete with the adsorptive properties of GAC for organic substrate, while literature sources (24, 111) indicate that the organic substrate may be competing with nonbiodegradable organics for adsorption sites on the GAC. To reduce the load on the GAC, and reserve most of the adsorption sites for organics which cannot be removed biologically, the biodegradable materials should be removed before contact with GAC.

This idea is in opposition to the theory of "BAC", which stresses that the organics must be adsorbed prior to biodegradation (112, 113). The demonstration of adsorbed biodegradable organics through dissolved oxygen demand on the warm contactor prior to reaching steady state TOC removal indicated that GAC could store biodegradable organics. The fact that the high dissolved oxygen demand could not be duplicated on the cold contactor when elevating its' temperature of operation suggested that acclimization was not allowing bacteria on GAC to degrade organics which would not be degraded on the sand contactor. The fact that the temperature change was imposed on the warm contactor while the TOC differential was still evident (without duplicating the high oxygen demand) indicated that bioregeneration (which would imply use of adsorbed organics and justify the concept of acclimization as an important mechanism) was not a significant mechanism. The reinstatement of a temperature induced TOC removal differential by returning to the warm-cold mode of operation confirmed that the differential was imposed by controlling the bacterial degradation rate of dissolved organics and not adsorbed organics.

Thus, bacteria attached to the GAC may not reduce the load of TOC to the GAC (prior to steady state) as well as bacteria which did not have to compete with adsorption, i.e., those attached to the sand. The consecutive unit processes of ozone, sand, and GAC may prove most advantageous in terms of reducing TOC. However, parallel studies discussed previously, investigating the use of GAC with or without preozonation on effluent from a rapid sand filter on a conventional treatment plant (i.e., including chlorination and the formation of THMs) suggest that ozonation may produce small uncharacterized organic molecules which compete with volatile organics of health concern (e.g. chloroform) for space on GAC.

Thses studies compared parallel GAC contactors receiving a common influent. The only difference in treatment was preozonation of the influent to one of the parallel contactors. The results indicated that the contactor receiving ozonated water had less capacity for chloroform and a much greater chromatographic displacement of chloroform into the effluent.

Careful investigation of the products of ozonation, and their interaction with specific organics, is required before ozonation is considered as a pretreatment for GAC applications.

This is suggested because chloroform was more poorly removed by parallel contactors receiving ozonated or nonozonated water from a common source. Therefore, the application of ozone to natural background organics for TOC removal should be characterized more completely as to the products of ozonation, and any ozone/GAC or ozone/sand/GAC application installed principally for the removal of volatile organics should carefully study the effects of ozonation of the natural organic matrix on the breakthrough profile of the contaminant to be removed prior to installing a full scale system.

Predicitive Models for Carbon Adsorption Design

The data evaluated in this study do not lead to a predicitive model of carbon contactor performance. However, a conceptual model of the mechanism of long term TOC removal was developed. The model indicates that adsorption and biodegradation proceed simultaneously on organics in the aqueous phase. Bacteria do not use adsorbed organics to an extent measurable by TOC. Long term removal is measurable by TOC, and is comprised of two components:

1) slow adsorption of organics in micropores as described by Peel and Benedek (20, 32) and Malleviälle (33)

2) biodegradation of organics in the aqueous phase

Carbon has been shown to store biodegradable material which can be acted on if the environmental conditions change. This was demonstrated in this study at low concentrations and data has been presented by Suidan (198) for much higher organic concentrations (i.e., 200 to 1000 mg/L) which can be interpreted in the same manner. The studies at high concentration were evaluated by a mass balance on carbon, organic and inorganic. The experiment increased the feed concentration (of catechol) in steps on the order of 100 mg/L or more per step. Over time, on a mass balance, all influent catechol was accounted for as methane and carbon dioxide in the effluent and there was little or no catechol retained on the GAC. However, there was always a lag between the stepwise increase in the influent concentration and the total carbon in the effluent. Furthermore, the effluent total carbon would exceed the influent after some time passed, indicating that the GAC was storing the catechol until the bacterial populations adjusted to the new feed concentration. Predictive models would need to take the storage phenomenon into account, particularly in waste treatment applications of high influent concentrations of organics which are both adsorbable and biodegradable.

To develop a predictive model of long term TOC removal, both adsorption and biodegradation should be taken into account. Both models will predict the breakthrough characteristics prior to steady state removal. This study has shown that adsorption can mask the effects of biodegradation almost to the point that steady state removal is achieved, therefore, the breakthrough characteristics are determined primarily from adsorption and do not depend on the parameters used to predict steady state removal.

SECTION 9

COST ANALYSIS

INTRODUCTION

Several advanced treatment schemes (Figure 197) were investigated to determine the economic feasibility of each to attain selected levels of organic removal at the Torresdale Water Treatment Plant. The results and operating parameters from the pilot-scale investigations were used as a basis for this economic feasibility study. The treatment processes investigated were: GAC alone, GAC preceeded by ozone (O_3/GAC), and ozone followed by sand filtration (O_3/SAND). Although both chlorinated and non-chlorinated systems were investigated, no consideration is given to any of the costs associated with modifications to the conventional treatment processes of the Torresdale Plant to allow for a non-chlorinated treatment process. For example, no consideration is given to any potential cost savings resulting from a lack of prechlorination. Alternatively, additional costs such as those which might be necessary in order to predisinfect the water with ozone or to cover the flocculation/sedimentation basins (in order to prevent excessive algae growth) are also not considered.

In order to calculate the total costs of each of the above treatment schemes, three unit processes were each examined separately to determine the capital and operational and maintenance (O & M) costs associated with each: GAC post-filtration contactors, GAC filter/adsorbers, and ozone generators and contactors. In addition, the costs associated with carbon regeneration and/or replacement were also examined. Due to the nature of the pilot-scale investigations, more consideration is given to the GAC post contactor mode of operation than the sand replacement, filtration/adsorption mode. This is because of evidence which suggests that this mode is 20-30% more efficient than the filter/adsorber mode for chloroform removal and 11-16% more efficient in terms of total organic carbon (TOC) removal (35). Furthermore, modifications to the Torresdale Plant rapid sand filters to GAC filter/adsorbers would result in an empty bed contact time of 13.8 minutes, which does not conform with the 15 and 30 minute EBCTs employed in the pilot scale investigations. It is only because of the extreme savings in capital costs associated with filter modification (relative to post contactor construction costs) which makes it absolutely necessary to at least present the estimated costs for the filter/adsorber operating mode.

ECONOMIC FACTORS

Cost estimates for the carbon adsorbers were calculated by the computer program described by Guarino, et al in Design and Economic Considerations of

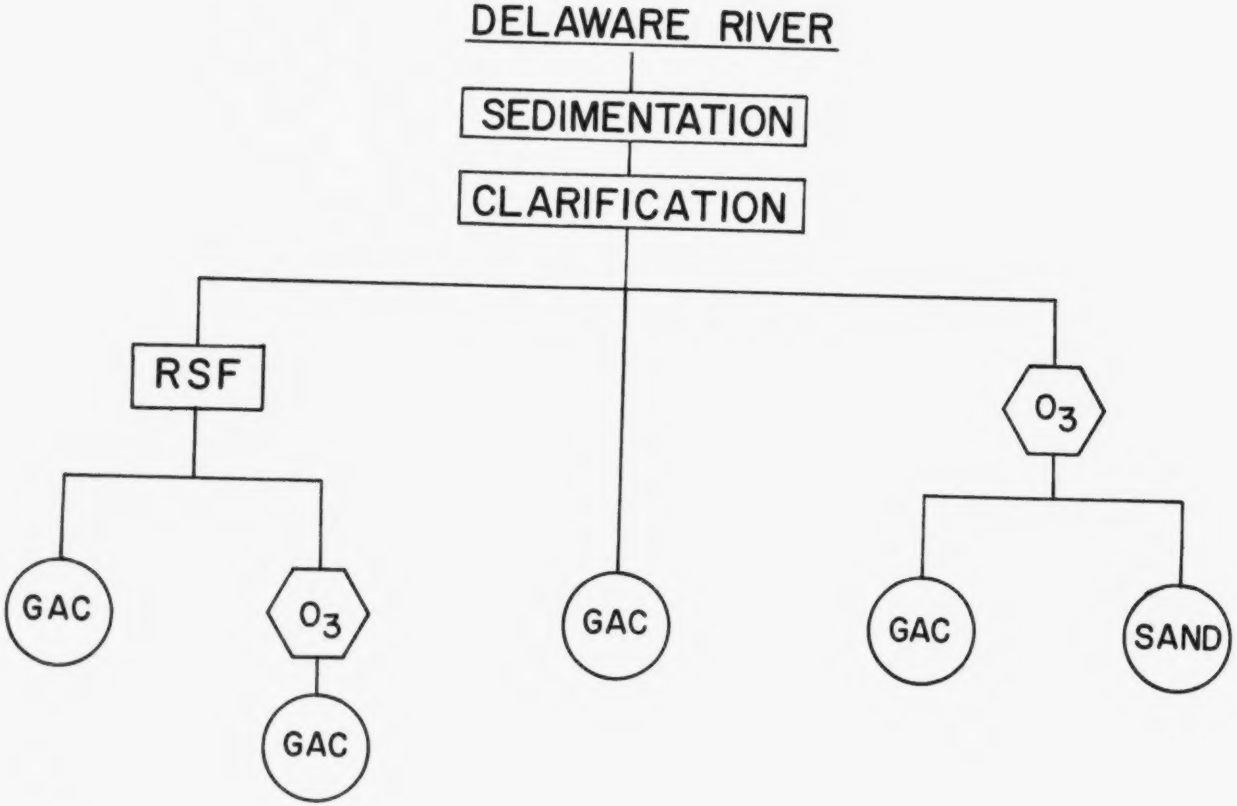
DELAWARE RIVER
SEDIMENTATION
CLARIFICATION
RSF
O_3
GAC
O_3
GAC
GAC
GAC
SAND

Figure 197. Advanced treatment alternatives.

Granular Activated Carbon Systems for Removal of Trihalomethanes and Synthetic Organic Contaminants (2). This computer program is a modified version of Computer Cost Models for Potable Water Treatment Plants (199) by Guttman and Clark. The ozone system operating and maintenance and capital costs were determined using information supplied by ozone equipment manufacturers and Estimating Water Treatment Costs (200) by Gumerman, et al.

All costs presented in this analysis are updated to 1981 dollars using the December 1981 ENR Construction Cost Index (CCI). This shows an increase of 42 percent over costs reported by Gumerman (200) in October, 1978 (CCI of 376 vs. 265). Inflation rates used in the calculation of the operating and maintenance costs were developed from the Wharton Econometrics Model (201).

The financial items used in this analysis are specific to the Philadelphia Water Department and represent the most recent data from the sale of revenue bonds. These bond issues are for 25 years duration at approximately 12% interest. The cost of securing the bonds has averaged about 40 percent of the capital required.

The Water Department obtains revenue from only 62 percent of the water treated. This is due to the loss of finished water in the distribution system. Factors contributing to this loss are: improper water meter registration, fire hydrant usage, and pipeline loss due to leakage and breaks. All costs reported in this section were calculated in terms of gallons of water treated.

DESIGN PARAMETERS

GAC System

Capital, operation and maintenance, and financial costs affecting the overall economics of a GAC facility are listed in Table 93. The GAC facilities investigated were based on a design flow of the Torresdale Plant of 282 MGD, EBCTs of 13.8 minutes (for the filter/adsorber mode) and 15 and 30 minutes (for the post contactor mode). Regeneration frequencies range from 1 month to 2 years to no regeneration at all.

Capital --

Post Contactor -- Table 94 lists the design criteria for the capital cost items necessary for both post contactor and filter/adsorber modes. The GAC post contactors were designed as common wall rectangular concrete boxes (20x40 foot) with a 10 foot carbon bed depth. For the 15 minute EBCT system, twenty five contactor pairs are required. Each is equipped with bottom air diffusers and hydraulic backwash systems to remove spent carbon. Troughs at the side of each contactor carry the carbon slurry to an automatic eductor system. An automatic carbon fill system is used to transport the regenerated carbon back to the carbon contactors. Low lift booster pumps are used to maintain a hydraulic head in the post contactor facility. A clear well was designed with a hydraulic capacity equal to that of the peak capacity of the Torresdale Plant (480 MGD).

Filter/Adsorber -- In modifying the existing sand filters for GAC, a maximum EBCT of 13.8 minutes is used due to current filter limitations. The gravel and sand filtration media is removed and an air diffuser system is placed over the leopold bottoms. Three layers of graded gravel is then followed by 45 inches of GAC. A 316 stainless steel mesh is placed over the gravel to prevent it from mixing with the carbon during backwash and removal. Fiberglass troughs at the sides of the filters carry away the spent carbon via an eductor system. The present backwash troughs will be raised to allow for the expansion of the carbon bed during backwashing. No pumping facility is necessary for the conversion of the sand filters to the filter/adsorber mode.

Carbon Regeneration and Storage -- The carbon regeneration facilities were designed to operate at 70% of their capacity. The extra capacity of these facilities handles the peak flows of the summer months. The hearth loading rates of the furnaces were set at 75 lbs/ft^2/day. Three furnaces have been specified, two of which operate during normal flow periods.

Shutdown, repair and startup of a furnace normally requires ten days for routine maintenance and/or minor breakdowns. Three storage facilities for GAC buffer stock, and spent and regenerated carbon each hold ten days of one furnace output. This is to be used in the event that a furnace becomes inoperable.

TABLE 93. GAC SYSTEM ECONOMIC FACTORS

CAPITAL

1. Carbon Contactors
2. Initial Carbon Fill
3. Backwash System
4. Regeneration Facility
5. Pumping Station and Hydraulic Modifications
6. GAC Makeup Storage
7. Laboratory Equipment

OPERATION and MAINTENANCE

1. Personnel
2. Power
    a. Regeneration Heat - 4250 Btu/lb. carbon
    b. Gas - \$5.09/10^6 Btu
    c. Regeneration Steam - 1 lb. Steam/lb. carbon
    d. Steam - \$13.50/1000 lb.
    e. Electric - \$0.056/Kwh
3. Materials
4. GAC Makeup

FINANCING

1. Bond Interest Rate-12%
2. Bond Issue Cost-40% of Capital
3. Amortization Period-25 Years

TABLE 94. CAPITAL COSTS - DESIGN CRITERIA

	Post Contactor		Filter/Adsorber
Pumping Station (MGD)	480	480	None Required (Gravity flow)
Contactors			
- Flow (MGD)	282	282	282
- EBCT (min.)	15	30	13.8
- Surface Loading Rate (gpm/ft^2)	4.9	4.9	2.0
- Surface Area per Pair (ft^2)	1600	1600	2088
- Number Contactor Pairs	25	50	47
- Contactor Construction	common wall concrete	common wall concrete	existing common wall concrete
Regeneration Facility			
- Number of Furnaces	3	3	3
- Hearth Loading Rate (lbs/ft^2/day)	75	75	75
- Furnace Capacity (lbs/day) (based on 6 months regeneration)	21,150	52,300	24,075

Operation and Maintenance --

Table 93 also presents the factors affecting the operation and maintenance of the GAC facilities. Required personnel include regeneration operators, maintenance mechanics, laboratory chemists and technicians, laborers and custodians. Power for the carbon regeneration process is necessary for transferring carbon to and from the furnaces and for the production of steam and/or heat necessary in the regeneration process.

Makeup carbon is another major contributor to the operation and maintenance costs. Typically, carbon losses vary from 5 to 15% but a properly designed furnace and carbon handling system can maintain losses at 7% (174). The effect of carbon loss on the cost of GAC system operation can be seen in Table 95. As either regeneration frequency or percent loss increase, the cost of GAC operation increases.

Initial carbon fill is based on the design flow of the Torresdale Plant (282 MGD) and the EBCT of the system. At $0.70/lb. (Calgon Filtrasorb 400), the carbon cost makes up a considerable portion of total capital costs. Competitive bidding by carbon manufactures could probably reduce these costs resulting in a more favorable comparison of carbon replacement versus regeneration.

TABLE 95. EFFECT OF CARBON LOSSES ON COSTS[1] OF GAC POST CONTACTOR

Carbon Losses (%)	Regeneration Frequency (Months)					
	1	3	6	12	18	24
6	1,759.9	886.8	661.3	548.6	511.0	491.5
7	1,814.4	904.9	670.2	553.1	514.0	493.7
8	1,868.8	923.1	679.2	557.6	517.0	495.9
9	1,923.2	941.2	688.2	562.0	520.0	498.2
10	1,977.7	959.4	697.1	566.5	523.0	500.4

---

[1] Total 25 year expenditures ($ Millions).

Ozone System

A partial failure in the ozone contacting systems during pilot scale testing (see DESCRIPTION OF STUDIES: Ozonation Systems) resulted in low ozone transfer efficiencies through both contactors. Satisfactory ozone residuals (0.3 mg/l) in the contactor effluent waters were maintained only through use of long ozone/water contact times (22 minutes) and high gas/liquid (G:L) ratios (> 4:1). In determining the full scale ozonation system costs, more standard values were used. Ozone generation requirements were estimated to average 2 mg/l (4700 lbs./day at a 1:1 G:L ratio) and ozone generator capacity was designed at 4 mg/l (9400 lbs./day). An ozone contact time of 20 minutes was used. This was followed by a holding tank (2 million gallons) which allowed 10 minutes for ozone residual dissipation.

Capital --

The ozone generators operated on a pure oxygen feed which was generated on site. Twelve ozone generators, each capable of producing 900 lbs/day, were specified. Capital costs incurred for the ozone equipment (Table 96) included oxygen and ozone generation equipment, dissolution equipment and related instrumentation. The cost of housing the equipment is also included in the capital costs.

Ozone contactor costs are based on information from Gumerman (200). The contact basins are covered reinforced concrete structures with depths of 18 feet and a length to width ratio of 2:1. Partitions within the basins assure uniform flow distribution.

TABLE 96. OZONE CAPITAL COSTS

	Ozone Generation Capacity-lbs/day		
	2350	4700	9400*
Ozone Equipment	$1,464,000	$2,928,000	$5,796,000
Housing	33,750	67,500	135,000
Ozone Contactors	1,260,680	1,260,680	1,260,680
Sub Total	2,758,430	4,256,180	7,191,680
Contingencies (15%)	413,765	638,427	1,078,752
Sub Total	3,172,195	4,894,607	8,270,432
Engineering (10%)	317,220	489,460	827,043
Total Capital	3,489,414	5,384,068	9,097,475
Bond Issue (Total Capital x 1.4)	4,885,180	7,537,695	12,736,465
Annual Amortized Capital Cost ($/yr) (25 years, 12%)	$ 622,860	$ 961,056	$1,623,900
¢/1000 Gal of Water Billed	1.0	1.5	2.6

*Used for calculating all ozone capital costs.

Operation and Maintenance --

Operation and maintenance costs (Table 97) for the ozonation system are also based on the work presented by Gumerman (200). Ozone generation rates are shown for dosages of 1, 2, and 4 mg/l at 1:1 G:L (2350, 4700, and 9400 lbs./day respectively). The costs are almost directly proportionate to output requirements. Building energy requirements include heating, cooling and lighting. Process power requirements consider oxygen and ozone generation as well as ozone dissolution (7.5 kwh/lb ozone produced).

TABLE 97. OZONE O & M COSTS

	Ozone Generation Rate (lbs/day)		
	2350	4700*	9400
O & M COSTS ($/yr)			
Energy[1]			
-Building	$ 4,200	$ 8,960	$ 17,920
-Process	360,255	720,510	1,441,020
-Total Energy	364,455	729,470	1,458,940
Labor[2]	36,000	63,000	127,500
Materials	14,640	29,280	57,960
Total First Year Costs	$415,095.	$821,750.	$1,644,400.
Ave. 25 Year Costs[3]	$1,632,929.	$3,232,656.	$6,468,853.

*Used in all O & M cost calculations.

[1] Energy Costs based on $0.056/kw-hr

[2] Labor costs @ $15./hr including fringe benefits.

[3] Average 25 year costs based on 10% annual inflation rate.

RESULTS

The costs associated with the ozone and GAC contacting systems are presented in Figures 198 to 200. These figures show annual amortized capital (25 years at 12%), first year operation and maintenance, and total first year costs, respectively. These costs are presented relative to carbon regeneration frequency. In general, as the period between carbon regenerations decrease, the costs increase. This is most evident for regeneration periods of six months and less. Ozonation system costs are independent of regeneration.

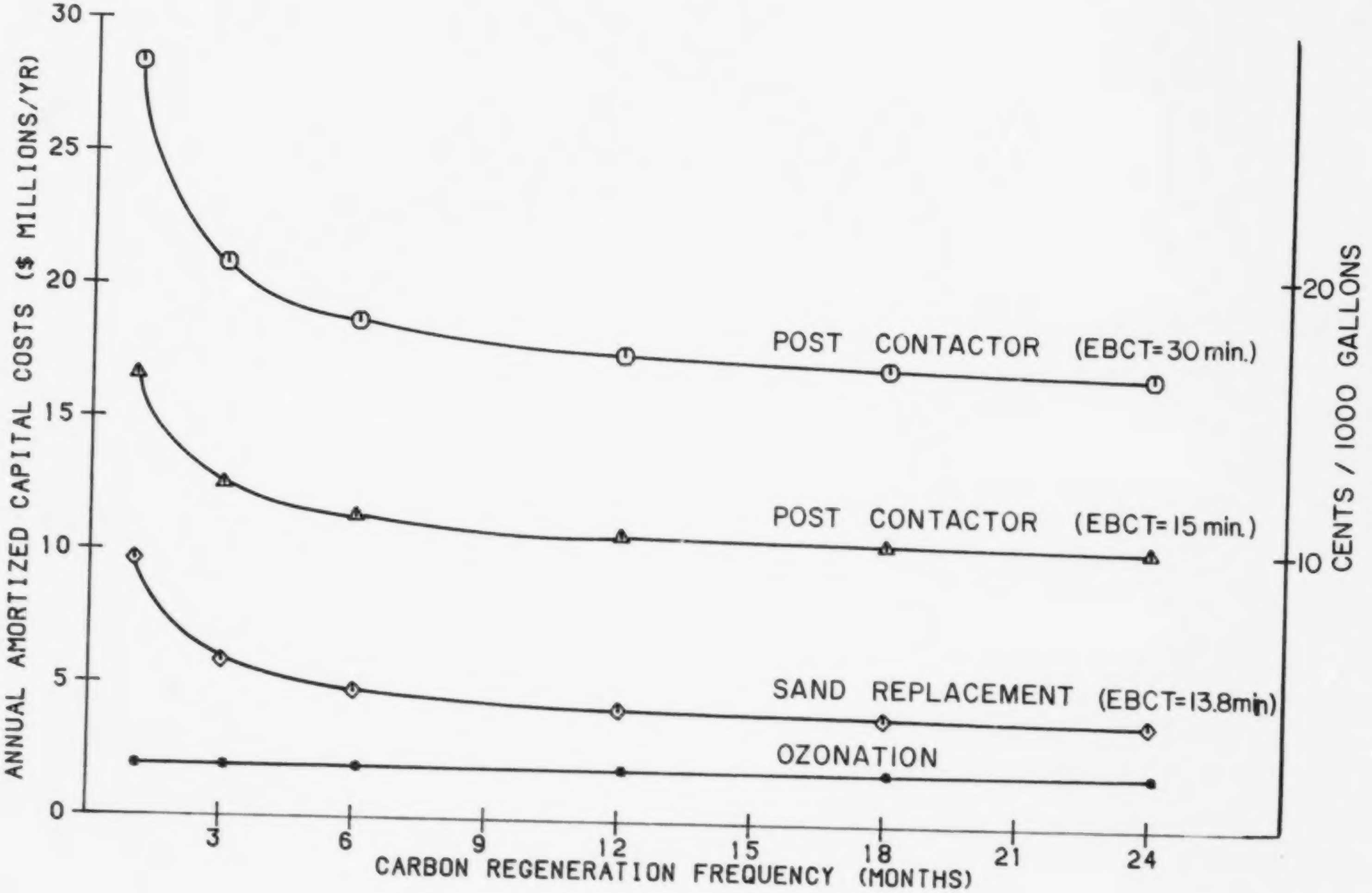

Figure 198. Annual amortized costs.

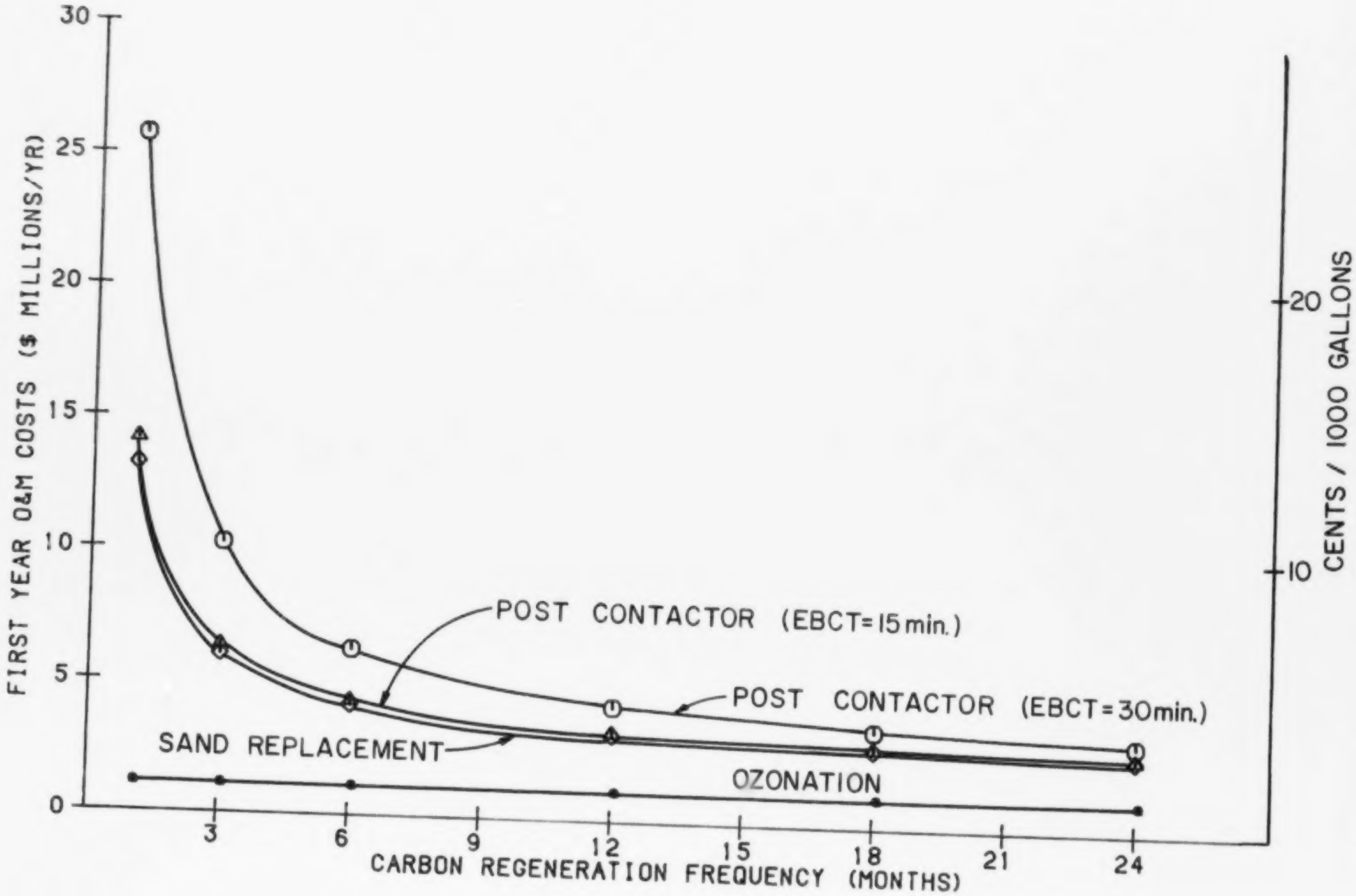

Figure 199. Operation and Maintenance costs (first year).

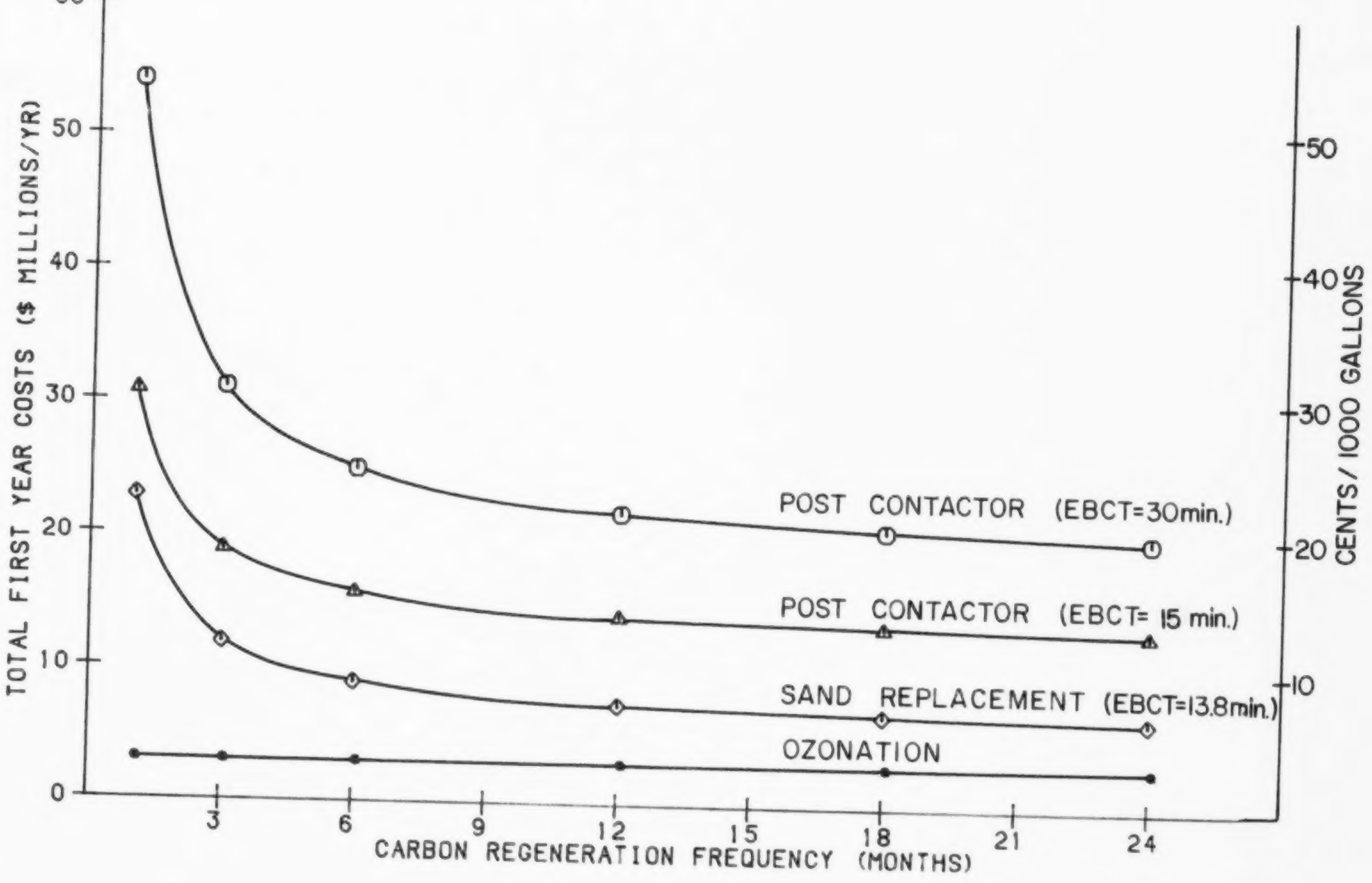

Figure 200. Total costs (first year).

The elements which comprise the capital costs of the 15 minute GAC post contactor system are shown in Table 98. Related first year operation and maintenance costs are shown in Table 99. The costs for each of the other advanced treatment systems utilize similar cost tables. Total first year costs (Figure 200) are the summation of annual amortized capital and first year operational and maintenance costs. As indicated in the figure, total first year costs for the sand replacement filter/adsorber mode are less than those for the post contactor mode. Various changes in the capital cost items contribute to this difference. For example, the sand replacement mode does not require an additional pumping station. Also, the cost of rapid sand filter modifications are minimal when compared to the cost of post contactor construction. Operation and maintenance costs for the 15 minute post contactor and sand replacement systems are, however, virtually identical.

When comparing the 15 and 30 minute post contactor systems, both capital and operation and maintenance items contribute to the increased costs associated with the increased contact time. A 30 minute system requires twice the number of contactors and initial carbon fill as a 15 minute system. This, in turn, will increase the size of the regeneration facility, as well as increasing the operation and maintenance items (regeneration power and makeup carbon) necessary for carbon regeneration.

DISCUSSION

Total first year costs (operation and maintenance plus amortized capital) for the GAC and O_3/GAC systems were developed based on the bed lives necessary to maintain various DOC, THMFP, Chloroform and DCP effluent criteria. The estimated annual costs to maintain specific DOC effluent criteria are shown in Tables 100 and 101. The annual costs are dependent on the carbon bed lives which are also shown in the tables. The point at which no regeneration is necessary was determined from data collected during the pilot studies. For example, Figure 201 shows the regeneration frequency needed to maintain different DOC criteria for the GAC_{15}(PP) and O_3/GAC_{15}(PP) systems. Since the maximum effluent DOC concentration observed for the systems were 1.9 ppm and 1.4 ppm respectively, any DOC criteria above these levels may be met without carbon regeneration. The level at which no regeneration is necessary is depicted by the dashed lines on the curves.

Figure 202 presents first year costs for the GAC(PP) and O_3/GAC(PP) systems at various DOC effluent limits (0.5 to 2.5 ppm). The solid lines denote the costs to maintain the criteria when carbon regeneration is necessary. Dashed lines represent the costs associated with no carbon regeneration. Figure 203 presents similar curves for the first year costs of the Torresdale Plant adsorption systems.

In general, the mode of contactor operation is a more significant cost determining factor than whether or not a system preozonates. In this context, the 30 minute post contactors were found to be the most costly system while the sand replacement filter/adsorbers were the least expensive. Again, care must be taken when comparing the filter/adsorber to the post contactor modes for the reasons outlined in the introduction to this section.

TABLE 98. CAPITAL COSTS-GAC POST CONTACTOP
TORRESDALE DESIGN FLOW -282 MGD-

I. Capital Cost Items

	Regeneration Frequency (Months) 1	3	6
A. Initial Carbon Fill	$7,000,000.	$7,000,000.	$7,000,000.
B. Pumping Station	$13,928,175.	$13,928,175.	$13,928,175.
C. Contactors (Gravity Feed)	$20,892,262.	$20,892,262.	$20,892,262.
D. Regeneration Facility	$24,895,175.	$10,608,449.	$6,449,996.
E. Carbon Unloading Facility	$14,626.	$14,626.	$14,626.
F. Carbon Handling System	$146,254.	$146,254.	$146,254.
G. Carbon Storage (Buffer)	$700,000.	$233,333.	$115,385.
H. Carbon Storage (Spent)	$2,210,821.	$736,940.	$364,421.
I. Carbon Storage (Regenerated)	$2,210,821.	$736,940.	$364,421.
J. Backwash Facility	$731,268.	$731,268.	$731,268.
K. Initial Materials	$143,793.	$143,793.	$143,793.
SUBTOTAL	$72,873,196.	$55,172,042.	$50,150,601.
CONTINGENCIES 15%	$9,880,980.	$7,225,807.	$6,472,590.
SUBTOTAL	$82,754,176.	$62,397,848.	$56,623,191.
ENGINEERING 10%	$8,275,417.	$6,239,784.	$5,662,319.
TOTAL CAPITAL	$91,029,593.	$68,637,633.	$62,285,510.
BOND ISSUE (x 1.4)	$127,441,430.	$96,092,686.	$87,199,714.
ANNUAL COSTS (25 YRS @ 12%)	$16,587,934.	$12,507,542.	$11,350,022.

TABLE 98 (CONT'D). CAPITAL COSTS-GAC POST CONTACTOR
TORRESDALE DESIGN FLOW -282 MGD-

I. Capital Cost Items

	Regeneration Frequency (Months) 12	18	24
A. Initial Carbon Fill	$7,000,000.	$7,000,000.	$7,000,000.
B. Pumping Station	$13,928,175.	$13,928,175.	$13,928,175.
C. Contactors (Gravity Feed)	$20,892,262.	$20,892,262.	$20,892,262.
D. Regeneration Facility	$4,187,713.	$3,378,914.	$2,941,057.
E. Carbon Unloading Facility	$14,626.	$14,626.	$14,626.
F. Carbon Handling System	$146,254.	$146,254.	$146,254.
G. Carbon Storage (Buffer)	$57,534.	$38,532.	$28,767.
H. Carbon Storage (Spent)	$181,711.	$121,697.	$90,856.
I. Carbon Storage (Regenerated)	$181,711.	$121,697.	$90,856.
J. Backwash Facility	$731,268.	$731,268.	$731,268.
K. Initial Materials	$143,793.	$143,793.	$143,793.
SUBTOTAL	$47,465,048.	$46,517,218.	$46,007,914.
CONTINGENCIES 15%	$6,069,757.	$5,927,583.	$5,851,187.
SUBTOTAL	$53,534,805.	$52,444,801.	$51,859,101.
ENGINEERING 10%	$5,353,480.	$5,244,480.	$5,185,910.
TOTAL CAPITAL	$58,888,286.	$57,689,281.	$57,045,011.
BOND ISSUE (x 1.4)	$82,443,600.	$80,764,993.	$79,863,015.
ANNUAL COSTS (25 YRS @ 12%)	$10,730,961.	$10,512,471.	$10,395,068.

TABLE 99. OPERATION AND MAINTENANCE COSTS-GAC POST CONTACTOR
TORRESDALE DESIGN FLOW -282 MGD-

II. O&M Costs-First Year

	Regeneration Frequency (Months)		
	1	3	6
A. Adsorber Labor	$371,735.	$371,735.	$371,735.
B. Adsorber Power	$960,000.	$960,000.	$960,000.
C. Adsorber Materials	$53,147.	$53,147.	$53,147.
D. Regeneration Labor	$704,805.	$704,805.	$704,805.
E. Regeneration Power	$568,792.	$189,597.	$93,757.
F. Regeneration Gas	$2,631,954.	$877,318.	$433,839.
G. Regeneration Steam	$1,642,500.	$547,500.	$270,742.
H. Regeneration Materials	$70,018.	$45,663.	$34,719.
I. Regeneration Outside Maint.	$995,807.	$424,338.	$258,000.
J. Make-up Carbon	$5,961,667.	$1,987,222.	$982,692.
K. Laboratory Labor	$186,200.	$186,200.	$186,200.
TOTAL ANNUAL O/M COSTS	$14,146,624.	$6,347,525.	$4,349,635.
ANNUAL AMORTIZED CAP. COSTS	$16,587,934.	$12,507,542.	$11,350,022.
TOTAL ANNUAL COSTS (CAP. & O/M COSTS)	$30,734,558.	$18,855,068.	$15,699,657.

TABLE 99 (CONT'D). OPERATION AND MAINTENANCE COSTS-GAC POST CONTACTOR
TORRESDALE DESIGN FLOW -282 MGD-

II. O&M Costs-First Year

	Regeneration Frequency (Months)		
	12	18	24
A. Adsorber Labor	$371,735.	$371,735.	$371,735.
B. Adsorber Power	$960,000.	$960,000.	$960,000.
C. Adsorber Materials	$53,147.	$53,147.	$53,147.
D. Regeneration Labor	$704,805.	$704,805.	$704,805.
E. Regeneration Power	$46,750.	$31,310.	$23,375.
F. Regeneration Gas	$216,325.	$144,878.	$108,163.
G. Regeneration Steam	$135,000.	$90,413.	$67,500.
H. Regeneration Materials	$26,483.	$22,658.	$20,223.
I. Regeneration Outside Maint.	$167,509.	$135,157.	$117,642.
J. Make-up Carbon	$490,000.	$328,165.	$245,000.
K. Laboratory Labor	$186,200.	$186,200.	$186,200.
TOTAL ANNUAL O/M COSTS	$3,357,954.	$3,028,468.	$2,857,790.
ANNUAL AMORTIZED CAP. COSTS	$10,730,961.	$10,512,471.	$10,395,068.
TOTAL ANNUAL COSTS (CAP. & O/M COSTS)	$14,088,914.	$13,540,939.	$13,252,858.

TABLE 100. ESTIMATED ANNUAL COST FOR TOC REMOVAL FROM PILOT PLANT EFFLUENT

	POST CONTACTOR				SAND REPLACEMENT	
	GAC_{15}(PP)	O_3/GAC_{15}(PP)	GAC_{30}(PP)	O_3/GAC_{30}(PP)	GAC_{15}(PP)	O_3/GAC_{15}(PP)
DOC ⩽ 0.5 ppm						
Bedlife (Days)	76	84	152	213	76	84
Annual Cost (mil)						
- First Year	20.0	21.9	26.2	26.7	12.9	14.9
- Average 25 Year	39.6	42.5	45.8	44.4	31.4	34.4
DOC ⩽ 1.0 ppm						
Bedlife (Days)	146	225	296	NR	146	225
Annual Cost (mil)						
- First Year	16.4	17.8	22.6	20.1	9.7	11.1
- Average 25 Year	29.0	31.1	35.2	26.2	21.6	23.2
DOC ⩽ 1.5 ppm						
Bedlife (Days)	258	NR	NR	NR	258	NR
Annual Cost (mil)						
- First Year	14.8	13.9	17.5	20.1	8.1	7.4
- Average 25 Year	24.1	19.9	21.3	26.2	17.1	13.4
DOC ⩽ 2.0 ppm						
Bedlife (Days)	NR*	NR	NR	NR	NR	NR
Annual Cost (mil)						
- First Year	11.3	13.9	17.5	20.1	4.8	7.4
- Average 25 Year	15.0	19.9	21.3	26.2	8.5	13.4

*NR-No Regeneration of carbon required to maintain effluent at this criteria.

TABLE 101. ESTIMATED ANNUAL COSTS FOR TOC REMOVAL FROM TORRESDALE PLANT EFFLUENT

	POST CONTACTOR				SAND REPLACEMENT	
	GAC_{15}(TP)	O_3/GAC_{15}(TP)	GAC_{30}(TP)	O_3/GAC_{30}(TP)	GAC_{15}(TP)	O_3/GAC_{15}(TP)
DOC ⩽ 0.5 ppm						
Bedlife (Days)	38	57	88	144	38	57
Annual Cost (mil)						
- First Year	27.0	24.9	31.4	26.7	19.5	17.7
- Average 25 Year	61.2	51.8	61.5	52.0	42.8	43.0
DOC ⩽ 1.0 ppm						
Bedlife (Days)	69	148	216	246	69	148
Annual Cost (mil)						
- First Year	20.7	29.0	24.1	26.0	13.6	12.3
- Average 25 Year	41.8	34.0	39.4	42.5	33.4	26.6
DOC ⩽ 1.5 ppm						
Bedlife (Days)	147	216	284	NR	147	216
Annual Cost (mil)						
- First Year	16.4	17.8	22.8	20.1	9.7	11.1
- Average 25 Year	29.0	30.2	35.6	26.2	21.6	23.1
DOC ⩽ 2.0 ppm						
Bedlife (Days)	219	NR*	NR	NR	219	NR
Annual Cost (mil)						
- First Year	15.2	13.9	17.5	20.1	8.5	7.4
- Average 25 Year	25.2	19.9	21.3	26.2	18.1	13.4

* NR - No regeneration of carbon required to maintain effluent at this criteria.

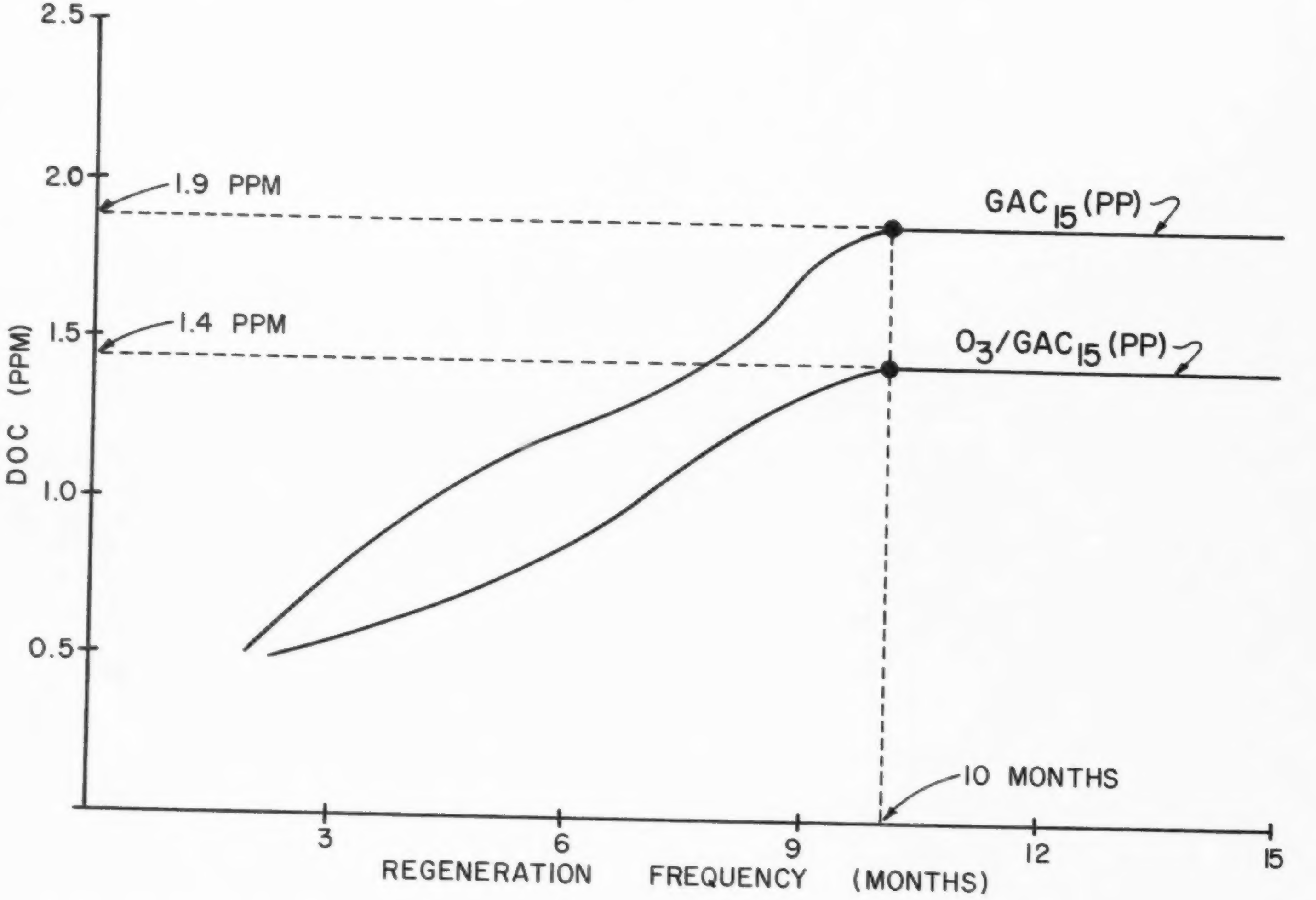

Figure 201. DOC levels for various regeneration frequencies.

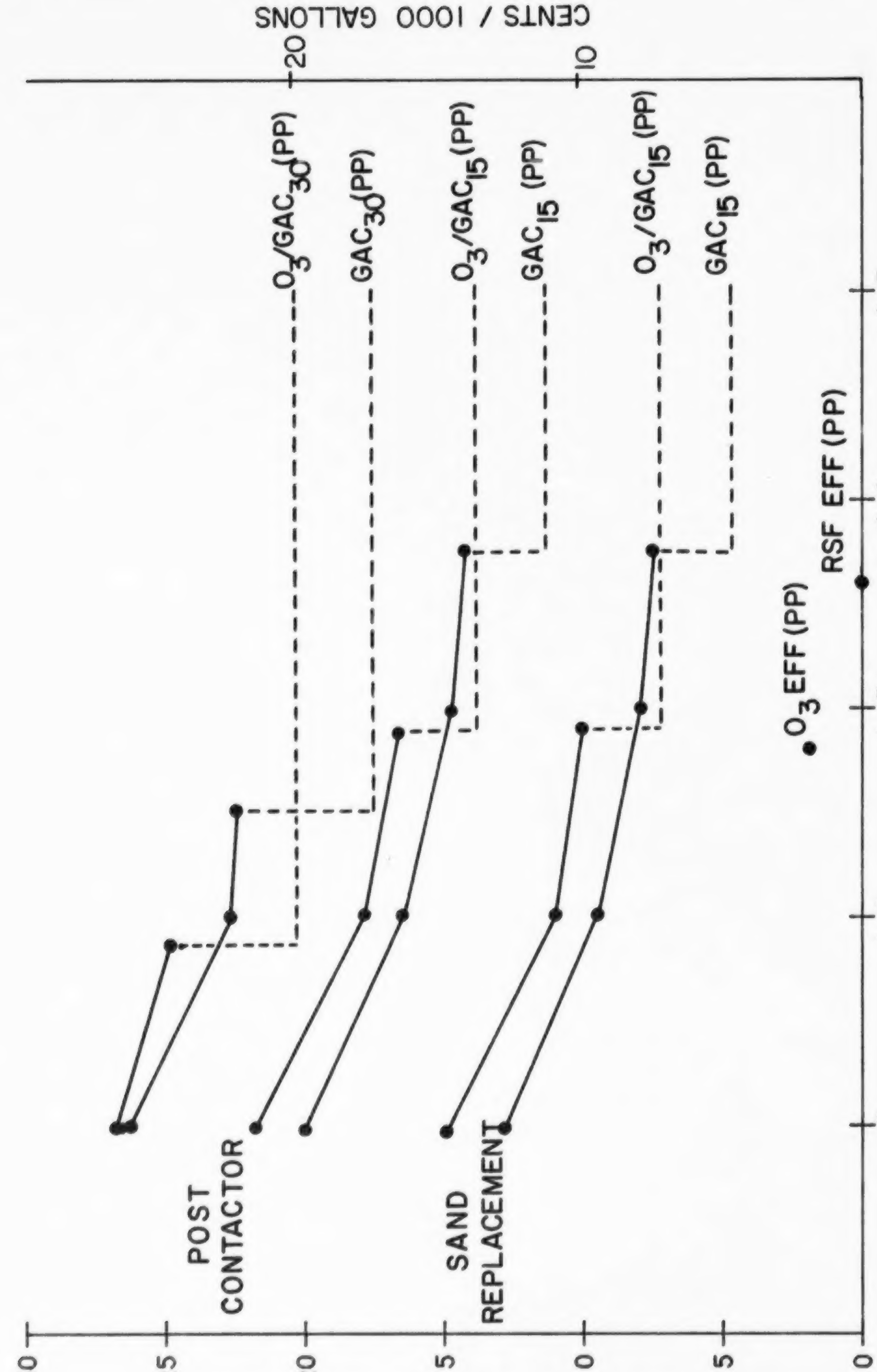

Figure 202. First year costs for DOC criteria (non-chlorinated).

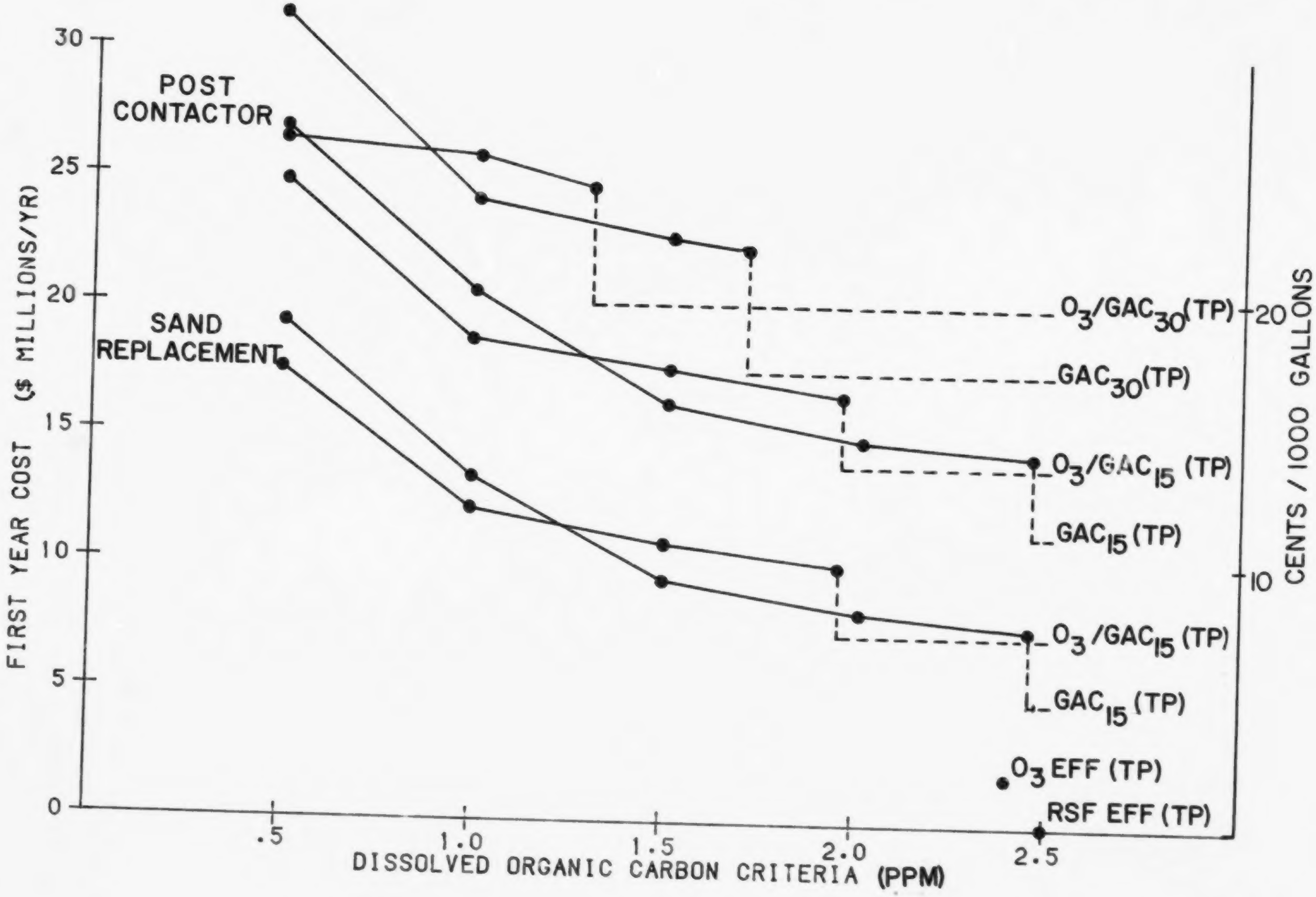

Figure 203. First year costs for DOC criteria (chlorinated).

For the Pilot Plant carbon systems, GAC alone was found to be less expensive than the comparable O_3/GAC system for most of the DOC effluent criteria. However, since preozonation did increase the removal of DOC at steady state, the level at which no carbon regeneration was required decreased from 1.8 to 1.4 ppm for the 15 minute EBCT systems and from 1.3 to 0.9 ppm for the 30 minute EBCT systems. Between these ranges, preozonation does result in a cost savings for GAC treatment.

For the Torresdale Plant systems, O_3/GAC was found to be more economical for most DOC criteria (Figure 203). In addition to where O_3/GAC is less costly due to increased steady state removal, O_3/GAC is also less costly at the lower DOC criteria. Preozonation results in a cost savings for the 15 minute EBCT systems for effluent criteria below 1.3 ppm or between 1.9 and 2.4 ppm; for the 30 minute EBCT systems, below 0.8 ppm or between 1.3 and 1.7 ppm.

In addition to the use of ozone in conjunction with GAC, the efficacy of an O_3/SAND system without GAC was also examined. From the results of the Pilot studies (see Table 52), an $O_3/SAND_{15}$ system (without prechlorination) was found to be capable of maintaining an effluent of 1.4 ppm DOC. Therefore, any effluent criteria above the 1.4 ppm DOC can be met through the use of ozone alone. The cost associated with this method of treatment is represented by the single point in the lower portion of Figure 202. Likewise, the Pilot Plant rapid sand filter effluent without any carbon or ozone treatment can maintain DOC levels of 1.8 ppm. This point is also shown in Figure 202; since there are no costs associated with this treatment method, the point falls on the x-axis.

A similar O_3/SAND system using Torresdale Plant water would not be as effective as the Pilot Plant O_3/SAND system was in reducing the DOC levels. This conclusion is drawn from our pilot studies which show that prechlorination results in less organic oxidation during ozonation (see Discussion Section). Furthermore, the free chlorine in the process water will effectively inhibit bacterial growth on a sand bed. As such, an O_3/SAND system in the Torresdale Plant would maintain an average effluent of 2.4 ppm, or just 0.1 ppm below what could be maintained without any advanced treatment.

The effect of inflation on the first year GAC and O_3/GAC costs is shown in Figure 204. Although the amoritized capital costs do not change from year to year, the operation and maintenance costs do become a greater and greater portion of the total system costs. This may result in a system which is initially O & M intensive to be cheaper in the short run, but in the long-term be the more expensive option. A comparison of total first year and average twenty-five year costs for the 15 minute post contacting system is shown in Figures 205 and 206 for the Pilot and Torresdale Plants, respectively. The average twenty-five year costs were developed by summing the total annual costs from year 1 to year 25 (based on a 10% inflation rate) and dividing by 25. The results of this comparison show that the basic relationships which were developed based on the first year costs hold when inflation is considered. The twenty-five year costs serve only to accentuate the observed patterns.

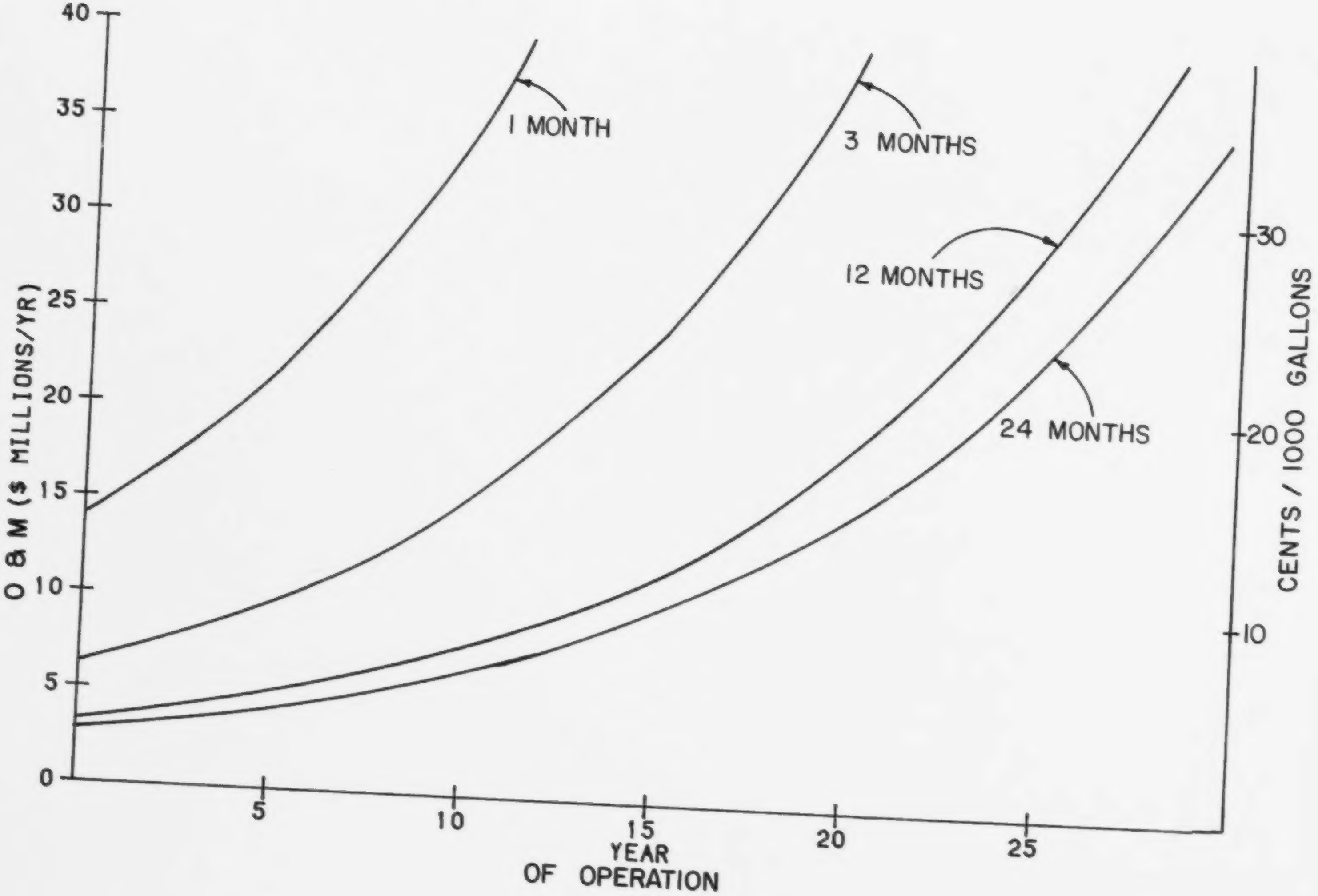

Figure 204. Effect of carbon regeneration frequencies on O & M costs.

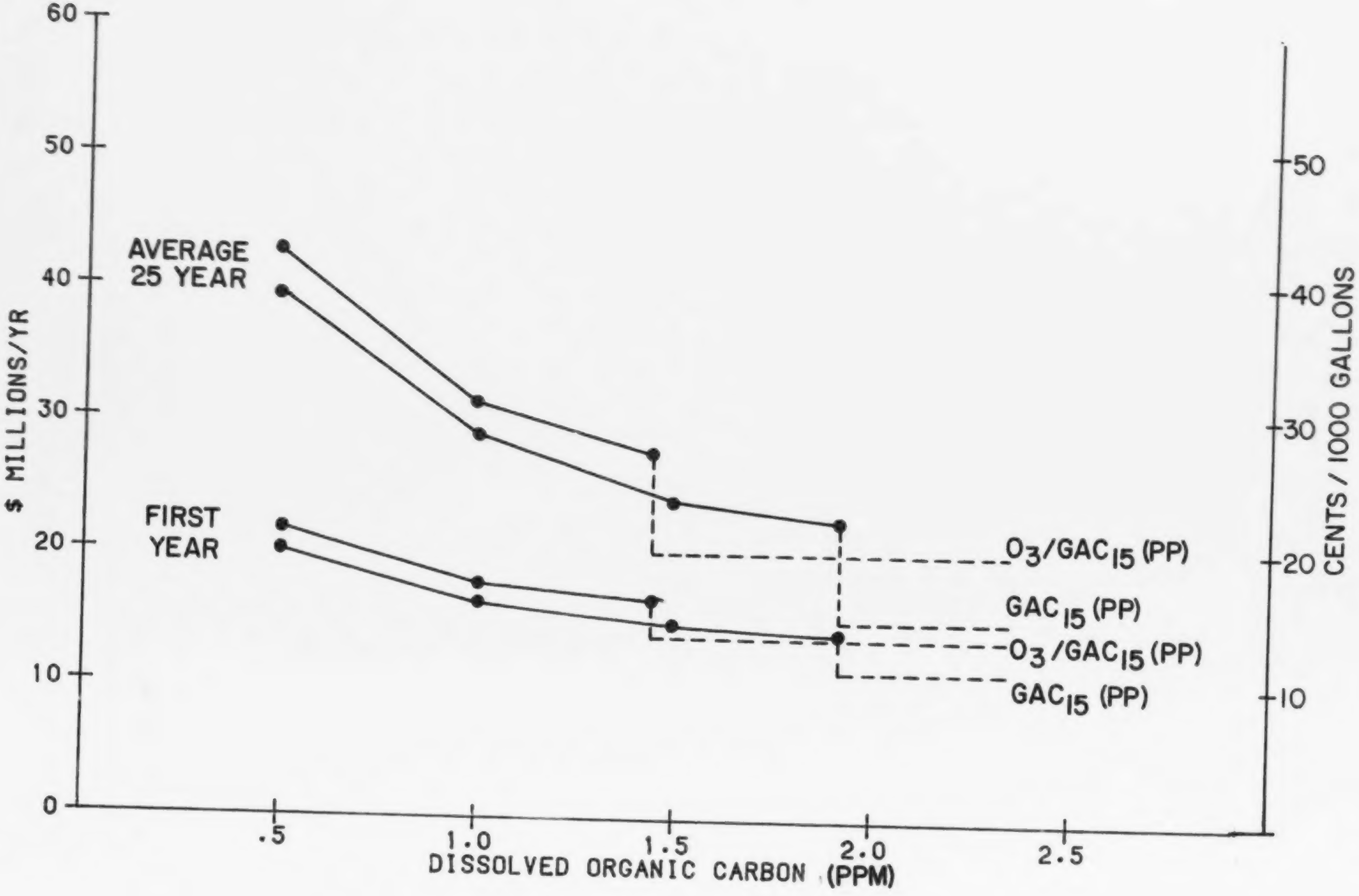

Figure 205. First year cost vs. average 25-year cost (non-chlorinated).

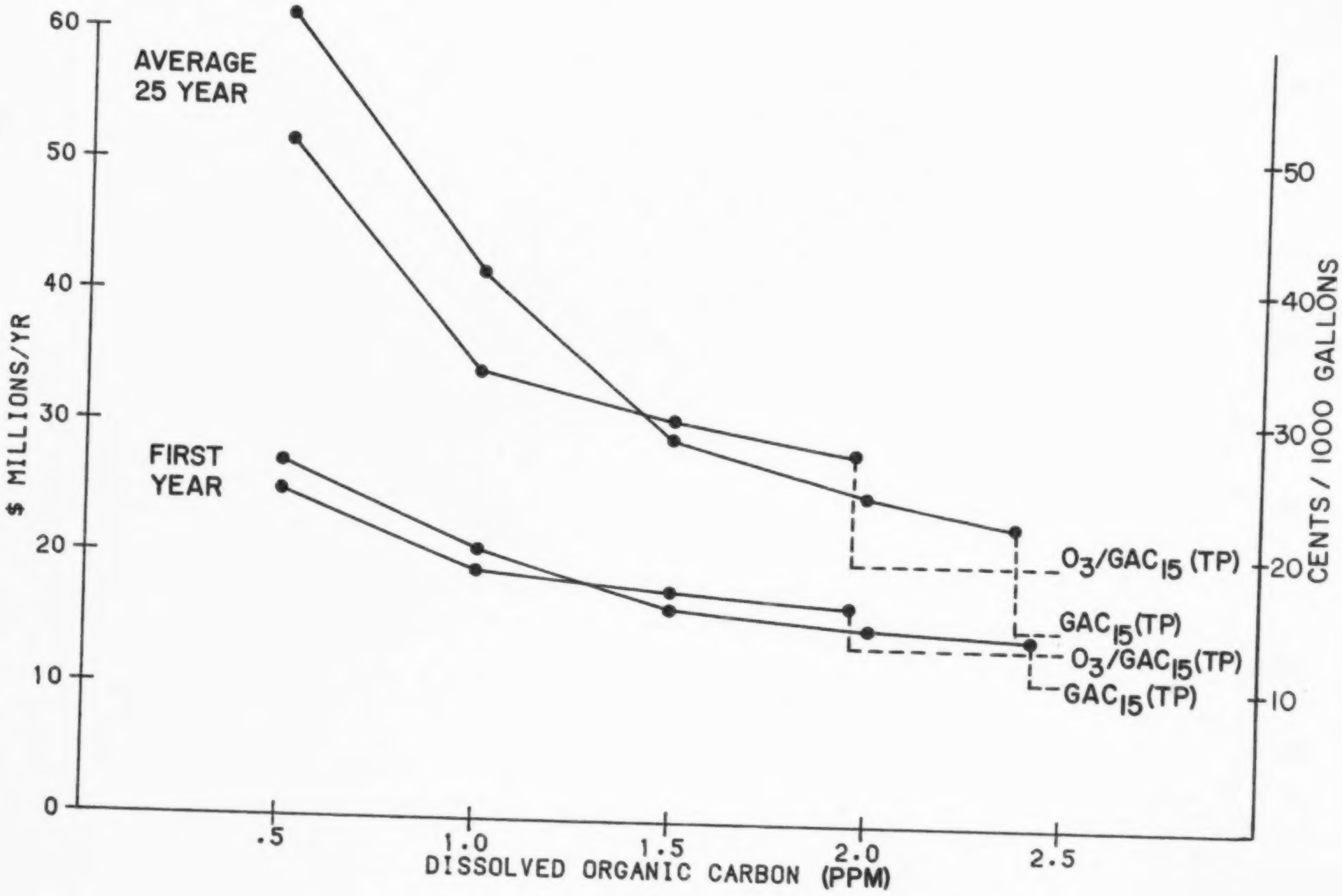

Figure 206. First year cost vs. average 25-year cost (chlorinated).

Cumulative mass loading data was also used as a basis for determining treatment costs. By finding the time to 50% removal on cumulative mass loading curves, the analysis is changed from one in which the criteria for bed life is based on the performance of a single filter to one which is based on the average output of any number of filters run in parallel. Results using this type of analysis is shown in Table 102 for 50% DOC removal and in Table 103 for 50% THMFP removal. The DOC results show that GAC alone is less costly than O_3/GAC. There is little difference between the chlorinated and unchlorinated waters.

The THMFP results show that there was an improvement in precursor removal costs when no prechlorination is used. Of special interest is the fact that the O_3/GAC(PP) system was able to maintain a 50% removal without carbon regeneration. This brought the first year system costs of the preozonated system to below those of the GAC system used alone.

Costs were also established for DCP removal based on effluent criteria of 1 and 5 ppb (Figure 207). As described in the Discussion Section of this report, the decreased loading of DCP onto the O_3/GAC bed (due to stripping in the ozone contactor) did not result in any notable increase in carbon bed life. This is reflected in the comparitive costs of GAC versus O_3/GAC. For all operating modes, the GAC System was found to be more economical than the O_3/GAC System.

When comparing the chlorinated Torresdale Plant system with that of the unchlorinated Pilot Plant, it appears that the unchlorinated system is less costly for removal of DCP. This may be misleading, however, since the Pilot Plant system generally had lower DCP loading rates than the Torresdale Plant system (presumably due to the different raw water intake systems used by the two plants, see DESCRIPTION OF STUDIES).

The final cost comparisons to be presented are based on chloroform effluent criteria of 1, 10, and 100 ppb. In general, the costs derived for chloroform are interchangeable with total trihalomethane costs since chloroform is the major constituent of the trihalomethanes and breakthrough is simultaneous. The costs are plotted in semilog form in Figure 208. As was shown for DCP, ozonation as a prelude to GAC treatment does not result in any cost savings when the removal of the halogenated, volatile organic compounds is used as the controlling criteria.

TABLE 102. CUMULATIVE MASS LOADING ANALYSIS

	Dissolved Organic Carbon			
	$GAC_{15}(PP)$	$O_3/GAC_{15}(PP)$	$GAC_{15}(TP)$	$O_3/GAC_{15}(TP)$
50% DOC Breakthrough (Days)	312	406	248	368
Mode				
Post Contactor ($ Millions)	14.3	16.6	14.8	16.6
Sand Replacement ($ Millions)	7.7	9.9	8.2	10.1

TABLE 103. CUMULATIVE MASS LOADING ANALYSIS

	Trihalomethane Formation Potential			
	$GAC_{15}(PP)$	$O_3/GAC_{15}(PP)$	$GAC_{15}(TP)$	$O_3/GAC_{15}(TP)$
50% THMFP Breakthrough (Days)	382	NR*	196	390
Mode				
Post Contacter ($ Millions)	14.0	13.9	15.5	16.6
Sand Replacement ($ Million)	7.4	7.4	8.8	10.0

* No Regeneration Required

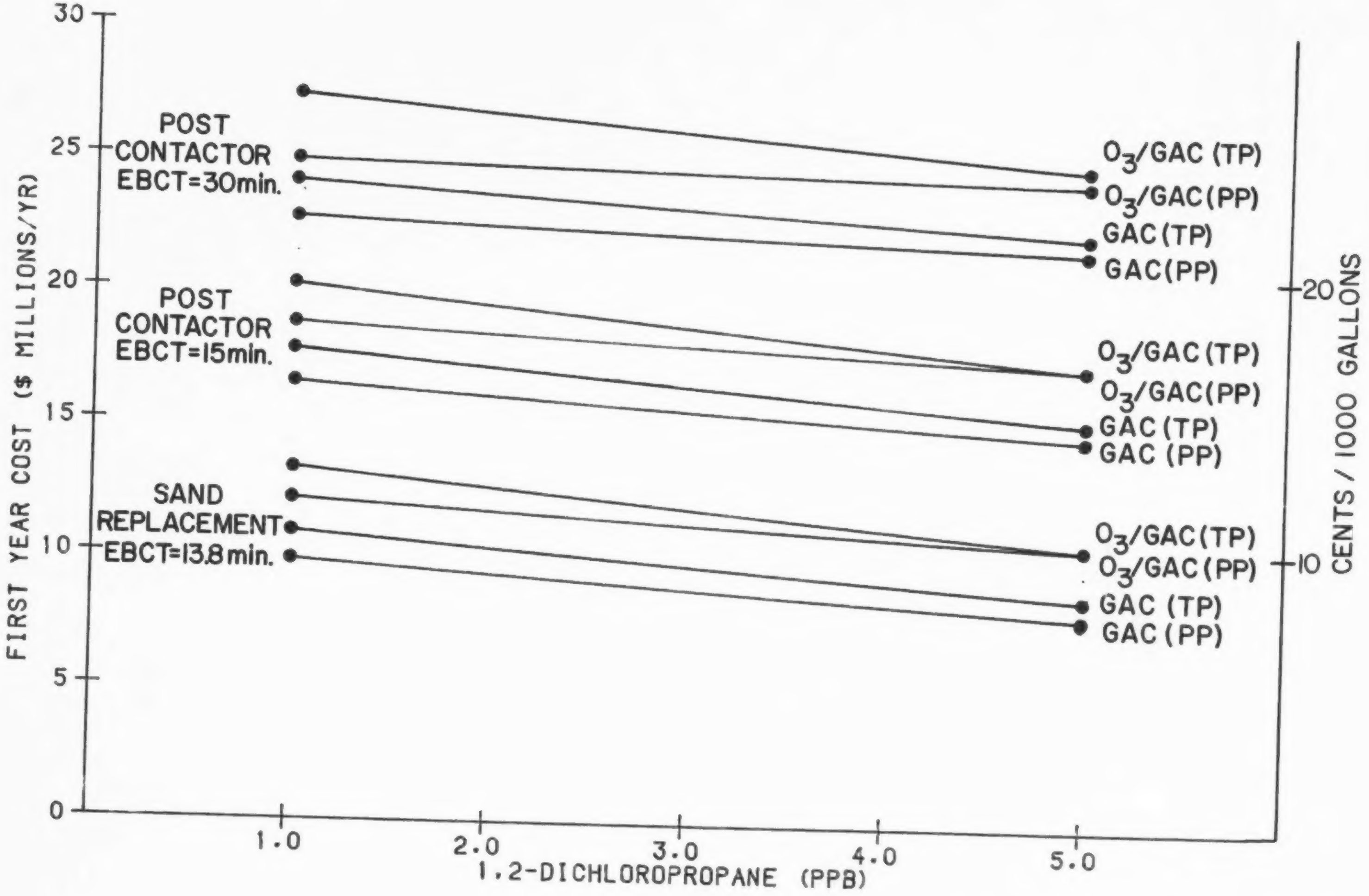

Figure 207. First year costs for 1,2-dichloropropane criteria.

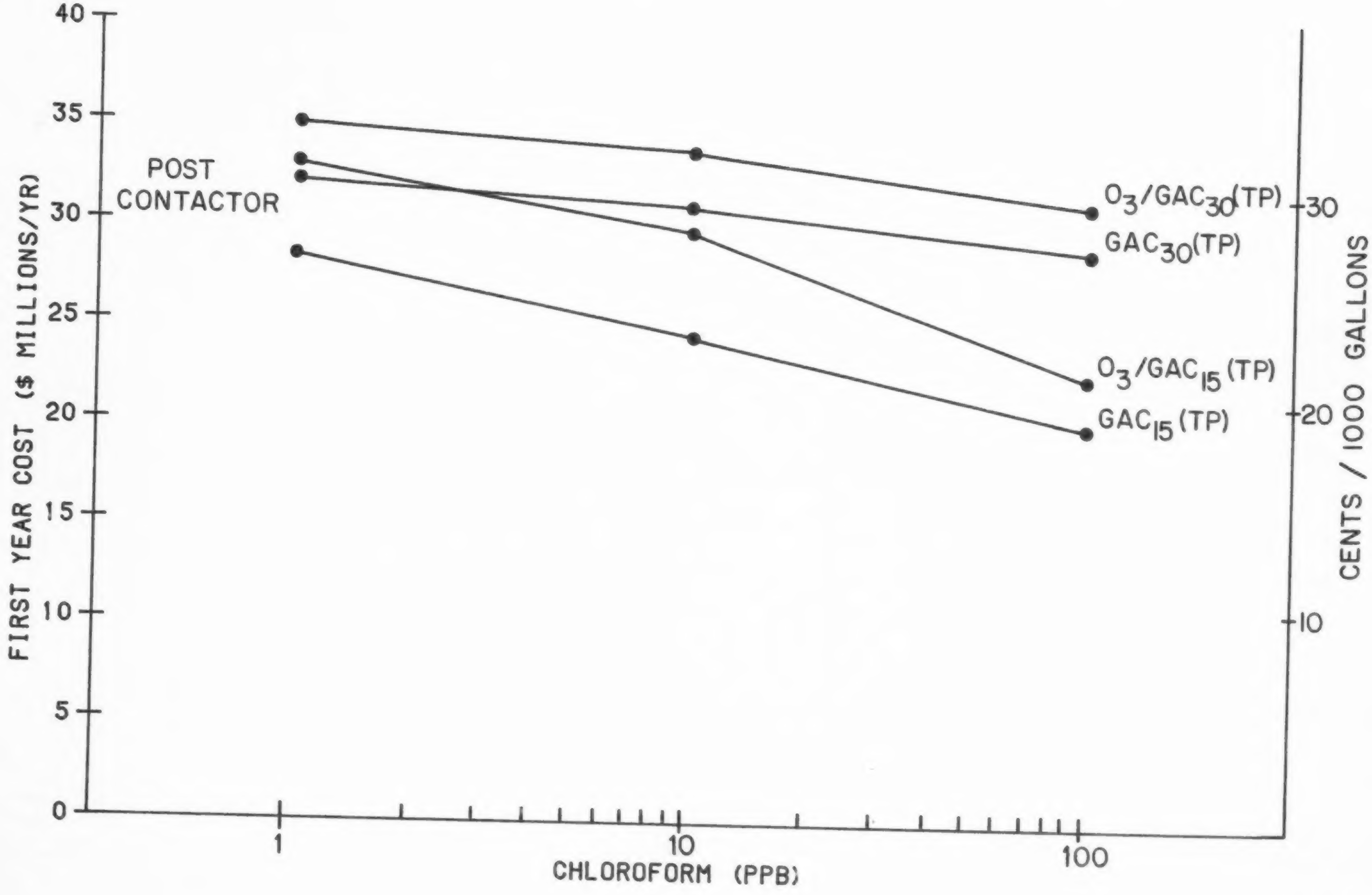

Figure 208. First year costs for chloroform criteria.

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APPENDIX A

QUALITY ASSURANCE FOR VOLATILE HALOGENATED AND NONHALOGENATED COMPOUNDS AS MEASURED BY THE PURGE AND TRAP METHOD.

INTRODUCTION

The quality assurance program that was used followed the principals outlined by the ACS Committee on Environmental Analytical Chemistry (A-1).

1. Maintenance of skilled personnel, written and validated methods, and properly constructed, equipped and maintained laboratory facilities
2. Provision of representative samples and controls
3. Use of high quality glassware, reagents and other testing materials
4. Calibration, adjustment and maintenance of equipment
5. Use of control samples and standard samples with proper records
6. Directly observing the performance of certain critical tests
7. Review and critique of results
8. Tests of internal and external proficiency testing
9. Use of replicate samples
10. Monitoring of results
11. Correction of departures from standards of quality

The quality assurance program included the following parts (A-2):

1. Reference Sample Analysis
2. Duplicate Analysis
3. Blind Sample Analysis
4. Stability of GC Retention Times
5. Confirmatory Analysis by GC/MS

Reference Sample Analysis

This section contains tables which summarizes the quality assurance data using external reference samples for purge and trap methods, TOC, TOX, CO_2, pH and turbidity. These reference samples were made in-house using organic free water and were run each day a sample was analyzed. Three reference standards for volatile halogenated compounds were used: a high range standard for chlorinated waters (Table A-1), a low range for non-chlorinated waters (Table A-2) and a very high range for trihalomethane formation potential work (Table A-3). The non-halogenated data is divided into two sections as a change was made to the USGS method in the later stages of the project

(Tables A-4 and A-5). All the data is within the criteria of 20% error above 10 ppb and 40% below 10 ppb utilized by the EPA for this type of analysis (A-2). The TOC data also falls within the criteria of 20 and 10%, respectively, for concentrations below and above 0.3ppm. Data for the other parameters is presented in Tables A-6 and A-7.

Duplicate Analysis

Five percent of all samples were analyzed in duplicate for halocarbons and TOC. Precision between duplicate values (calculated as the absolute value of their difference, divided by their average, times 100) was determined for each pair of data and the mean precision and standard deviation calculated for each parameter. The results of these calculation are given for the halocarbons in Tables A-8 to A-10 for three concentration ranges. Results for TOC are given in Table A-11 for two concentration ranges. The results are 10% higher than the range of the data reported by Kinsley et al. (A-2).

Blind Sample Analysis

Laboratory proficiency has been tested externally by EPA for volatile organic analysis over the course of the project by taking part in the EPA laboratory certification program. In order to qualify for certification, blind samples (samples of unknown concentration) are analyzed and the results are reported to EPA. The laboratory is certified only if all results fall between certain established accuracy limits. The Organics Laboratory has participated in five certifications over the course of the project. The results of the tests are listed in Tables A-13 to A-17. The certification procedure has been a very valuable part of the quality assurance program. In one instance in February 1980 the laboratory did not pass certification and the cause of failure was traced to new reagents of questionable purity. This situation was corrected immediately and in the November 1980 certification testing the error was less than 10% in all cases. It should be noted that in 1980 the EPA certification acceptance limits for trihalomethanes were changed from a 95% confidence interval limit to an absolute limit of ± 20% error as specified in the SDWA trihalomethane regulations.

Stability of GC Retention Times

Relative retention data for GC and GC/MS analyses were shown in Table 35. The stability of GC retention times was closely monitored over the course of the project to insure proper compound identification. The stability was found to be excellent as seen in Table A-12 which contains retention time data for standards covering a period of four weeks on both the halogenated and nonhalogenated systems. The standard division of all retention times was <0.16.

Confirmatory Analysis by GC/MS

GC/MS confirmatory analysis was performed on thirteen samples. The results are presented in Tables A-18 and A-19. The values listed in parentheses on these tables were found in the GC analysis. Positive identification means the compound was confirmed by both mass spectral data and relative retention time data versus a standard. Tentative identification indicates GC/MS mass spectral confirmation without retention time data. Fifty percent of the compounds identified by GC were confirmed by GC/MS. Over 85% of the non-confirmed GC peaks were less then 1 ppb and at the limit of GC/MS detection. In cases above the limit of detection (at values >10 ppb for acetone and 1 ppb for all other compounds) confirmation was positive in 52 out of 53 cases. Fifteen volatile organics has been positively identified by GC/MS.

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A-2. Kingsley, B. et al. in Vol 2, Advances in the Identification and Analysis of Organic Pollutants in Water, edited by L.H. Keith, Ann Arbor Science Publ./The Butterworth Group, Ann Arbor Mich.

TABLE A-1. VOLATILE HALOGENATED QUALITY ASSURANCE (HIGH RANGE)

Compound	True Values	Avg.	Number of Data Points	Std. Dev.	CV[1]	% Error[2]	Range	
							Min.	Max.
MECL	2.2	1.6	34	0.6	38	27	0.8	3.4
CHLO	75	73	37	7.6	10	3	60	93
DCE2	2.4	2.3	37	0.2	9	4	2.0	2.9
TCE1	2.4	2.2	37	0.4	18	8	1.5	3.1
CTET	2.4	2.1	37	0.5	24	13	1.5	3.7
DCBM	23	22	37	1.9	9	4	19	28
DCP2	3.0	2.8	37	0.4	14	7	2.1	3.8
TCE	2.3	1.9	38	0.4	21	17	1.2	3.5
DBCM	5.4	5.0	38	0.8	16	7	2.6	6.3
BROM	2.3	2.2	38	0.2	9	4	1.7	2.6
PER	2.3	2.3	38	0.7	30	0	1.5	5.1
BCEE	4.1	2.9	37	1.2	41	29	0.5	5.7
CBEN	2.4	2.4	38	0.7	29	0	1.1	4.9

[1] Coefficient of Variation (% S.D.): Standard Deviation divided by the average times 100.

[2] Difference between the absolute value of the true value and average found concentration, divided by the true concentration times 100.

TABLE A-2. VOLATILE HALOGENATED QUALITY ASSURANCE (LOW RANGE)

Compound	True Value	Avg.	Number of Data Points	Std. Dev.	CV[1]	% Error[2]	Range Min.	Range Max.
MECL	0.4	0.4	67	0.2	50	0	0.1	1.1
CHLO	7.5	8.2	78	1.3	16	9	5.6	11.0
DCE2	0.5	0.4	78	0.1	25	20	0.3	0.6
TCE1	0.5	0.4	77	0.1	25	20	0.3	0.8
CTET	0.5	0.4	78	0.1	25	20	0.3	0.9
DCBM	2.3	2.3	78	0.3	13	0	1.6	3.4
DCP2	0.6	0.6	77	0.1	17	0	0.4	0.8
TCE	0.5	0.4	78	0.1	25	20	0.3	0.7
DBCM	1.1	1.0	78	0.2	20	9	0.4	1.4
BROM	0.5	0.4	78	0.1	25	20	0.3	0.5
PER	0.5	0.4	78	0.1	25	20	0.3	0.8
BCEE	0.8	0.6	69	0.3	50	25	0.1	2.3
CBEN	0.5	0.4	78	0.1	25	20	0.1	0.9

[1] Coefficient of Variation (% S.D.): Standard Deviation divided by the average times 100.

[2] Difference between the absolute value of the true value and average found concentration, divided by the true concentration times 100.

TABLE A-3. VOLATILE NON-HALOGENATED QUALITY ASSURANCE DATA (1)

Compound	True Value	Avg.	Number of Data Points	Std. Dev.	CV[1]	% Error[2]	Range	
							Min.	Max.
ACET	4.3	3.5	35	1.8	51	19	0.4	9.2
DMM	1.3	1.4	35	0.6	43	8	0.2	3.1
BEN	1.2	1.1	34	0.2	18	8	0.7	1.5
TOL	1.2	1.1	35	0.3	27	8	0.5	1.4
EBEN	1.2	1.0	35	0.2	20	17	0.4	1.3
CUM	1.2	1.1	35	0.2	18	8	0.5	1.5
XYL2	1.2	1.2	34	0.2	17	0	0.5	1.5
XYL3	1.5	1.6	27	0.2	13	7	1.3	1.9
DCB2	1.7	1.3	26	0.1	8	23	1.1	1.6

[1] Coefficient of Variation (% S.D.): Standard Deviation divided by the average times 100.

[2] Difference between the absolute value of the true value and average found concentration, divided by the true concentration times 100.

TABLE A-4. VOLATILE NON-HALOGENATED QUALITY ASSURANCE DATA (2)

Compound	True Value	Avg.	Number of Data Points	Std. Dev.	CV[1]	% Error[2]	Range	
							Min.	Max.
ACET	4.3	3.8	19	0.9	24	12	2.0	5.6
DMM	1.3	1.2	19	0.2	17	8	0.7	1.6
BEN	1.2	1.4	17	0.3	21	17	1.0	2.0
TOL	1.2	1.3	19	0.2	15	8	1.0	1.6
EBEN	1.2	1.2	19	0.2	17	0	0.7	1.6
CUM	1.2	1.3	19	0.2	15	8	0.9	1.6
XYL2	1.2	1.3	19	0.2	15	8	0.9	1.6
XYL3	1.5	1.8	18	0.5	28	20	1.3	3.4
DCB2	1.7	1.7	19	0.3	18	0	1.1	2.5

[1] Coefficient of Variation (% S.D.): Standard Deviation divided by the average times 100.

[2] Difference between the absolute value of the true value and average found concentration, divided by the true concentration times 100.

TABLE A-5. THMFP QUALITY ASSURANCE DATA

Compound	True Value	Avg.	Number of Data Points	Std. Dev.	CV[1]	% Error[2]	Range Min.	Range Max.
CHLO	151	150	124	12	8	1	116	180
DCBM	47	46	124	4.4	10	2	36	64
DBCM	11	11	124	0.8	7	0	8.7	13
BROM	4.6	4.5	124	0.4	9	2	3.5	5.5

TABLE A-6. NON-SPECIFIC ORGANIC QUALITY ASSURANCE DATA

Parameter	True Value	Avg.	Number of Data Points	Std. Dev.	CV[1]	% Error[2]	Range Min.	Range Max.
TOC from 8/17/80	1600	1617	119	58	4	1	1447	1711
TOX	5000	5041	33	343	7	1	4509	5869

[1] Coefficient of Variation (% S.D.): Standard Deviation divided by the average times 100.

[2] Difference between the absolute value of the true value and average found concentration, divided by the true concentration times 100.

TABLE A-7. INORGANIC QUALITY ASSURANCE DATA

Parameter	True Value	Avg.	Number of Data Points	Std. Dev.	CV[1]	% Error[2]	Range Min.	Range Max.
CO_2	50	54	25	5.9	11	8	42	64
pH	8.5	8.5	191	0.1	1	0	8.2	8.7
Turbidity	1.80 NTU	1.76	43	0.03	2	2	1.71	1.84

[1] Coefficient of Variation (% S.D.): Standard Deviation divided by the average times 100.

[2] Difference between the absolute value of the true value and average found concentration, divided by the true concentration times 100.

TABLE A-8. PRECISION OF DUPLICATE ANALYSIS (Concentration < 1 PPB)

Compound	No. of Duplicate Positives[1]	Mean % P[2]	S.D[2]
Methylene chloride	43	27	28
Chloroform	10	18	20
1,2-Dichloroethane	47	15	23
1,1,1-Trichloroethane	30	12	25
Carbon Tetrachloride	5	14	29
Dichlorobromomethane	30	12	21
1,2-Dichloropropane	18	26	27
Trichloroethylene	33	15	26
Dibromochloromethane	16	3	5
Bromoform	44	5	21
Tetrachloroethylene	31	11	19

[1] Number of times this compound was found at or above the quantification limit in both analysis.

[2] % Precision was calculated for each pair as 100 times their difference divided by their average. The mean and standard deviation (S.D.) of these values were then calculated.

TABLE A-9. PRECISION OF DUPLICATE ANALYSIS (Concentration >1 PPB and <10 PPB)

Compound	No. of Duplicates[1]	Mean % P[2]	S.D.[2]
Methylene chloride	0		
Chloroform	28	9	10
1,2-Dichloroethane	15	14	15
1,1,1-Trichloroethane	0		
Carbon Tetrachloride	0		
Dichlorobromomethane	6	17	12
1,2-Dichloropropane	41	9	10
Trichloroethylene	0		
Dibromochloromethane	49	6	5
Bromoform	10	10	10
Tetrachloroethylene	0		

[1] Number of times this compound was found at concentrations between 1 and 10 PPB.

[2] % Precision was calculated for each pair as 100 times their difference divided by their average. The mean and standard deviation (S.D.) of these values were then calculated.

TABLE A-10. PRECISION OF DUPLICATE ANALYSIS (CONCENTRATION > 10 PPB)

Compound	No. of Duplicates[1]	Mean % P[2]	S.D.[2]
Methylene chloride	0		
Chloroform	67	8	8
1,2-Dichloroethane	0		
1,1,1-Trichloroethane	0		
Carbon Tetrachloride	0		
Dichlorobromomethane	67	7	7
1,2-Dichloropropane	3	11	6
Trichloroethylene	0		
Dibromochloromethane	18	9	9
Bromoform	0		
Tetrachloroethylene	0		

[1] Number of times this compound was found in concentrations higher than 10 PPB.

[2] % Precision was calculated for each pair as 100 times their difference divided by their avera ge. The mean and standard deviation (S.D.) of these values were then calculated.

TABLE A-11. PRECISION OF DUPLICATE TOC ANALYSES

Concentration	No. of Duplicates	Mean % P[1]	S.D.[1]
500PPB	5	7	6
500PPB	122	3	3

[1] Precision is calculated for each pair as 100 times their difference divided by their average. The mean and standard deviation (S.D.) of these precision values were then calculated.

TABLE A-12. GC RETENTION TIME STABILITY DATA

Compound	No. of Analysis	Mean Retention Time (Minutes)	RRT of the Mean
Methylene Chloride	14	5.37 ± 0.09	0.46[1]
Chloroform	14	11.75 ± 0.10	1.00
1,2-Dichloroethane	14	12.68 ± 0.10	1.08
1,1,1-Trichloroethane	14	14.15 ± 0.10	1.20
Carbon Tetrachloride	14	14.60 ± 0.10	1.24
Dichlorobromomethane	14	15.32 ± 0.09	1.30
1,2-Dichloropropane	14	16.80 ± 0.09	1.43
Trichloroethylene	14	17.74 ± 0.09	1.51
Dibromochloromethane	14	18.49 ± 0.09	1.57
Bromoform	14	21.44 ± 0.09	1.82
Tetrachloroethylene	14	23.87 ± 0.10	2.03
Chlorobenzene	14	26.59 ± 0.11	2.26
Bis(2-chloroethyl) ether	14	27.62 ± 0.12	2.35
Acetone	11	7.53 ± 0.05	0.72[2]
Dimethoxymethane	11	9.18 ± 0.05	0.88
Benzene	11	13.68 ± 0.02	1.31
Toluene	11	18.58 ± 0.03	1.77
Ethylbenzene	11	23.41 ± 0.06	2.24
Cumene	11	27.78 ± 0.08	2.65
m-Xylene	11	31.07 ± 0.10	3.22
o-Xylene	11	32.90 ± 0.12	3.14
Dichlorobenzene	11	42.24 ± 0.16	4.03

[1] Relative Retention Time versus Chloroform (11.75 minutes) for the period 7/15/81 to 8/15/81.

[2] Relative Retention Time versus Chloroform (10.47 minutes) for the period 9/15/81 to 10/15/81.

TABLE A-13. EPA CERTIFICATION RESULTS - MARCH 1979

Compound	True Value	Analysis Value	% Error	EPA Evaluation	Acceptance Limits[1]
CHLO	22.8	34	49	Acceptable	0-45
CHLO	91.3	116.6	28	Acceptable	30-137
CTET	4.2	6.6	57	Acceptable	0-13
CTET	16.8	23.6	40	Acceptable	0-43
DCBM	2.4	4.4	83	Acceptable	0-8.2
DCBM	23.8	29.6	24	Acceptable	0-56
TCE	1.9	2.4	26	Acceptable	0-6.4
DBCM	2.1	1.8	14	Acceptable	0.1-3.4
DBCM	10.3	9.7	6	Acceptable	0-17
BROM	2.8	3.1	11	Acceptable	0-6.0
BROM	11.4	12.1	6	Acceptable	0.7-21
PER	1.8	3.3	83	Acceptable	0-4.5
DCE2	2.1	2.7	29	Acceptable	0-5.9
DCE2	17.3	20.5	18	Acceptable	4.2-33

[1] The acceptance limit is a 95% confidence interval calculated from available certification data from EPA and state laboratories.

TABLE A-14. EPA CERTIFICATION RESULTS - APRIL 1979

Compound	True Value	Analysis Value	% Error	EPA Evaluation	Acceptance Limits[1]
CHLO	74.6	104	39	Acceptable	21 - 117
CHLO	11.2	19.1	70	Acceptable	2.4 - 21
DCBM	51.9	61.0	17	Acceptable	16 - 76
DCBM	9.4	11.8	26	Acceptable	1.6 - 16
DBCM	11.3	13.7	21	Acceptable	0 - 30
DBCM	45.2	54.0	19	Acceptable	5.1 - 85
BROM	32.7	32	2	Acceptable	3.3 - 58
BROM	8.2	9.3	13	Acceptable	2.1 - 14

[1] The acceptance limit is a 95% confidence interval calculated from certification data from EPA and state laboratories.

TABLE A-15. EPA CERTIFICATION RESULTS - FEBRUARY 1980

Compound	True Value	Analysis Value	% Error	EPA Evaluation	Acceptance Limit[1]
CHLO	7.46	10.5	41	Unacceptable	6.0 - 9.0
CHLO	93.2	82.6	11	Acceptable	75 - 110
DCBM	42.5	21.7	51	Unacceptable	34 - 51
DCBM	4.72	3.0	36	Unacceptable	3.8 - 5.7
DBCM	17.0	16.7	2	Acceptable	14 - 20
DBCM	50.9	39.4	23	Unacceptable	41 - 61
BROM	81.8	86.4	7	Acceptable	65 - 98
BROM	12.3	10.5	15	Acceptable	9.8 - 15

[1] The acceptance limit is the true value ± 20%.

TABLE A-16. EPA CERTIFICATION RESULTS - NOVEMBER 1980

Compound	True Value	Analysis Value	% Error	EPA Evaluation	Acceptance Limit[1]
CHLO	14.9	15.9	7	Acceptable	12 - 18
CHLO	44.7	43.1	4	Acceptable	36 - 54
DCBM	94.4	90.8	4	Acceptable	76 - 110
DCBM	18.9	18.6	2	Acceptable	15 - 23
DBCM	11.3	10.9	3	Acceptable	9.0 - 14
DBCM	84.8	76.2	10	Acceptable	68 - 100
BROM	24.5	26.4	8	Acceptable	20 - 29
BROM	61.4	57.8	6	Acceptable	49 - 74

[1] The acceptance limit is the true value ± 20%.

TABLE A-17. EPA CERTIFICATION RESULTS - APRIL 1981

Compound	True Value	Analysis Value	% Error	EPA Evaluation	Acceptance Limit[1]
CHLO	76.6	81.2	6	Acceptable	61 - 92
CHLO	10.2	10.7	5	Acceptable	8.2 - 12
DCBM	91.2	87.9	4	Acceptable	73 - 110
DCBM	22.8	22.5	1	Acceptable	18 - 27
DBCM	71.1	65.0	9	Acceptable	57 - 85
DBCM	11.8	10.9	8	Acceptable	9.4 - 14
BROM	98.7	95.8	3	Acceptable	79 - 120
BROM	32.9	32.9	0	Acceptable	26 - 39

[1] The acceptance limit is the true value ± 20%.

TABLE A-18. GC/MS IDENTIFICATION DATA[1]

COMPOUND	RRT[2]	4/15/80		7/14/80	7/28/80		9/22/80	
		O_3C(TP)	O_3RT(TP)	O_3RT(PP)	RSF(PP)	O_3RT(PP)	RSF(TP)	O_3RT(TP)
MEC1	0.61	P(0.6)[3]	P(0.4)	-(BD)[4]	-(0.1)	-(BD)	P(0.1)	P(BD)
CHLO	1.00	P(63)	P(61)	P(1.4)	P(0.9)	P(1.4)	P(115)	P(73)
DCE2	1.06	-(0.2)	P(0.1)	P(2.5)	P(0.5)	P(2.3)	P(0.9)	-(0.7)
TCE1	1.17	P(BD)	-(BD)	-(BD)	-(0.1)	-(BD)	-(0.1)	-(BD)
CTET	1.19	-(BD)	-(BD)	-(BD)	-(BD)	-(BD)	-(0.3)	-(0.1)
DCBM	1.23	P(13)	P(13)	P(0.3)	-(0.1)	-(0.3)	P(37)	P(26)
DCP2	1.33	P(0.1)	P(0.1)	P(2.4)	P(3.7)	P(2.3)	P(2.0)	P(1.8)
TCE	1.40	P(0.2)	P(0.2)	-(0.2)	-(BD)	-(0.3)	-(0.2)	-(0.5)
DBCM	1.45	P(1.9)	P(1.6)	-(0.1)	-(BD)	-(0.1)	P(8.9)	P(7.5)
BROM	1.68	-(BD)	-(BD)	-(BD)	-(0.1)	-(BD)	-(0.5)	-(0.4)
PER	1.87	P(0.1)	-(0.1)	-(BD)	-(BD)	-(BD)	-(0.7)	-(0.1)
CBEN	2.07	-(BD)	-(BD)	-(BD)	-(BD)	-(BD)	-(1.3)	-(0.5)
ACET	0.66	P(7.5)	P(11)	-(3.2)	-(2.0)	-(9.1)	P(21)	P(44)
DMM	0.82	-(BD)	-(BD)	-(3.4)	-(6.4)	-(3.2)	-(0.5)	-(BD)
BEN	1.42	P(0.1)	P(0.1)	-(0.4)	-(0.3)	-(0.4)	-(0.2)	-(0.2)
TOL	1.98	P(1.2)	P(0.7)	-(0.2)	-(0.1)	-(0.5)	-(0.2)	-(BD)
EBEN	2.24	-(0.2)	-(0.1)	-(BD)	-(BD)	-(BD)	-(BD)	-(BD)
THF	0.92	T	-	-	-	-	-	-
ET_2O	0.98	T	-	-	-	-	-	T
MEK	1.04	-	T	-	-	-	-	-

1. Analysis performed on a Finnigan 4021 GC/MS/DS. Mass Range Scanned: 33-300 amu. Scan Rate: 33-300 amu/1.95 second.

2. Relative retention time versus chloroform (absolute retention time of 15.9 minutes) using an 8 ft x 2mm ID glass column packed with 1% SP-1000 on Carbopack B (60/80 Mesh). Carrier gas: Helium at 20 mL/min. Oven Program: 45°C (4 minute hold) to 220°C at 6°C/min.

3. The number in parenthesis is the quantified value by GC analysis.

4. BD is below detectable limits. For GC/MS analysis this will vary due to daily sensitivity fluctuations from 0.1 to 1.0 ppb for all compounds except for ACET and DMM where it varies from 5 to 10 ppb.

T = tentitive identification - GC/MS only.
P = positive identification - GC/MS and GC retention time.

THF - Tetrahydrofuran
ET_2O - Ethyl ether
MEK - Methyl ethyl ketone

TABLE A-19. GC/MS IDENTIFICATION DATA[1]

COM-POUND	RRT[2]	10/6/80	11/10/80		1/13/81	9/29/81	10/6/81
		O_3/GAC(PP)	RSF(PP)	O_3RT(PP)	O_3RT(TP)	RSF(PP)	O_3RT(PP)
MECL	0.61	P(0.1)[3]	P(0.2)	P(0.1)	P(0.3)	P(0.1)	P(0.4)
CHLO	1.00	P(7.3)	P(1.9)	P(1.7)	P(17)	P(2.6)	P(2.2)
DCE2	1.06	P(0.9)	P(1.1)	P(1.0)	P(3.9)	P(1.0)	P(0.5)
TCE1	1.17	P(0.1)	P(0.1)	P(0.1)	P(0.1)	-(0.1)	P(0.2)
CTET	1.19	-(0.1)	-(BD)[4]	-(BD)	P(0.3)	-(BD)	P(0.3)
DCBM	1.23	P(1.0)	P(0.6)	P(0.6)	P(6.5)	P(0.9)	P(1.1)
DCP2	1.33	P(1.1)	P(6.9)	P(5.2)	P(22)	P(1.8)	P(1.3)
TCE	1.40	-(BD)	P(0.3)	-(0.1)	P(0.6)	P(0.2)	-(0.2)
DBCM	1.45	-(BD)	-(0.2)	-(0.2)	P(2.1)	-(0.3)	P(0.4)
BROM	1.68	-(BD)	-(BD)	-(BD)	-(0.2)	-(BD)	-(BD)
PER	1.87	-(0.1)	P(BD)	-(BD)	P(0.3)	P(0.2)	P(0.3)
CBEN	2.07	-(BD)	P(1.3)	P(0.3)	P(0.3)	-(BD)	P(0.3)
ACET	0.66	P(0.8)	-(1.7)	P(12)	P(100)	P(3.9)	P(89)
DMM	0.82	-(2.2)	T(15)	T(9.7)	-(1.1)	-(8.9)	T(3.5)
BEN	1.42	P(0.1)	P(0.1)	P(0.1)	P(0.7)	-(4.0)	P(1.5)
TOL	1.98	P(BD)	P(0.1)	P(BD)	P(1.9)	-(0.5)	P(0.3)
EBEN	2.24	-(BD)	-(BD)	-(BD)	P(0.2)	-(BD)	P(BD)
THF	0.92	-	-	-	-	-	-
ET_2O	0.98	-	-	-	T	-	T
MEK	1.04	-	-	-	-	-	-

1. Analysis performed on a Finnigan 4021 GC/MS/DS. Mass Range Scanned: 33-300 amu. Scan Rate: 33-300 amu/1.95 second.

2. Relative retention time versus chloroform (absolute retention time of 15.9 minutes) using an 8 ft x 2mm ID glass column packed with 1% SP-1000 on Carbopack B (60/80 Mesh) Carrier gas: Helium at 20 mL/min. Oven Program: 45°C (4 minute hold) to 220°C at 6°C/min.

3. The number in parenthesis is the quantified value by GC analysis.

4. BD is below detectable limits. For GC/MS analysis this will vary due to daily sensitivity fluctuations from 0.1 to 1.0 ppb for all compounds except for ACET and DMM where it varies from 5 to 10 ppb.

T = tentitive identification - GC/MS only.
P = positive identification - GC/MS and GC retention time.

THF - Tetrahydrofuran
ET_2O - Ethyl ether
MEK - Methyl ethyl ketone

APPENDIX B

QUALITY ASSURANCE OF MACRORETICULAR RESIN (MRR) SAMPLERS IN TRACE ORGANIC ANALYSIS

INTRODUCTION

Macroreticular resin (MRR) samplers are widely used to collect ng/l quantities of trace organics from water. Yet, few studies present quality assurance data to establish confidence in the experimental results. This appendix attempts to define the precision of the MRR sampling and chromatographic analyses used in this report. This appendix analyzes both the overall results and individual analysis protocol steps to gain a better understanding of this sampling and concentration technique. To accomplish this, two 3-day on-line composite sampling runs were carried out in this program within a water treatment pilot plant setting. An XAD-2/XAD-8 mixed resin bed was used in the experimental design shown in Figure B-1.

XAD-2 is a non-polar stryene/divinyl benzene copolymer. XAD-8 is a methylmethacrylate polymer and is slightly more polar than XAD-2. Each exhibits a different adsorption selectivity due to structural and polarity differences. The physical characteristics of XAD-2 and XAD-8 are shown in Table B-1.

1) Characterization of the Background Organic Chemicals Leaching From the Resins During Cleanup/Preparation of Resin (Resin Cleanup)

The cleaning procedure of Junk et al (B-1) was used for the macroreticular resins. It included soxhlet extraction of the two types of resin (XAD-2 and XAD-8) for 24 hours each by methanol, acetonitrile and ethyl ether. During each soxhlet step, a blank and waste solvent sample were taken and analyzed by capillary gas chromatography. Subsequently, the waste solvent was analyzed by GC/MS and potential resin sampler artifacts tentatively identified.

2) Ether Elution Efficiency of Resin Samplers (Ether Extraction Efficiency)

Solvent and sampler blanks were collected before each run. Subsequent comparison of blanks and samples allowed subtraction of possible contamination biases from results due to solvents, resin breakdown, etc. The efficiency of the ether extraction was checked by a fourth elution after the extraction of samples which consisted of 3 consecutive elutions of 150, 100 and 100 mL.

TABLE B-1. PHYSICAL PROPERTIES OF XAD RESINS[a]

PROPERTY	XAD-2	XAD-8
Porosity[b] (ml pore/ml bead)	0.42	0.50-0.54
Surface Area (m^2/g)[b]	300	140
Average Pore Diameter (Angstrom)[b]	90	250
True Wet Density in Distilled Water (g/mL)	1.02	1.05
Bulk Density (lbs/ft^3)	40	43
Particle Size (Mesh)	20-60	20-60

[a] Rohm and Haas Corporation, Philadelphia, Pa.

[b] Dry Basis

3) Reproducibility Between Samples Collected by the MRR Accumulators (Sample Reproducibility)

A reproducibility study was performed in which five MRR samplers received the same influent water. A blank elution and recleaning of the sampler was completed prior to collecting a three day composite sample. The sample was then eluted and concentrated for capillary gas chromatographic analysis in the same manner as all other samples.

The data from the first composite run were used to study the reproducibility of the sampling method. The precision of data from the five replicate samplers were compared to form a model of the causes of variations in peak response

4) Breakthrough of Organics Occuring in MRR Accumulators (Resin Sampler Breakthrough)

The combined XAD-2/XAD-8 resin beds have a volume of approximately 200 mL. Because water flows through the bed at approximately 35 mL/min for 3 days there is a possibility of breakthrough of organic solutes. The experimental design of the breakthrough columns is identical to the method used for the samplers. Two 3-day on-line composite sampling runs of 131-156 L were carried out in this study. The effect of pH and DOC loading of the resins were evaluated.

5) Evaluation of Base Extraction Cleanup of the Ether Extract of the Resin (Base Extraction)

Base extraction was developed to make the ether elutions from the resin accumulators compatible with capilary gas chromatography. Therefore, an ether extract sample was split to determine the effects of base extraction on the nonpolar organics. The two samples were analyzed by GC and GC/MS. The total number of peaks affected by the base extraction were determined and tentatively identified by GC/MS.

LITERATURE REVIEW

Nearly from their advent by Kunin (B-2, B-3), nonionic macroreticular resins were used to adsorb water soluble organic species (B-4). Osterroht (B-5) developed a method of extracting volumes of seawater on XAD resin for the determination of non-polar dissolved organic substances. The application of macroreticular resins to drinking water begins with the work of Junk (B-1, B-6). Junk et al (B-1) established the basis of the now widely used resin cleaning procedure which was used in the present study. Also in 1974, Musty and Nickless (B-7) used macroreticular resins for extraction and recovery of chlorinated pesticides and polychlorinated biphenyls. By 1976, resins were being used by Leenheer and Hoffman (B-8) to extract and fractionate organic solutes from water. Fritz (B-9), Aiken, Thurman and Malcolm and Coworkers (B-10, B-11) were extensively involved with the study of adsorption of natural organics onto, and the capacity factors of XAD resins. The capacity factors determined at the U.S. Geological Survey by Leenheer, Aiken and Coworkers (B-10 to 13) were applied to adsorption studies in this project.

To summarize, MRR's tend to preferentially select solutes on the basis of polarity, steric effects, molecular size, solubility and diffusion velocity. Competition between chemical species for adsorption sites, although not widely investigated in the literature, is a particular problem in natural and treated water sampling. The four major factors influencing the capacity for adsorption by competing species in a resin bed are: inherent surface capacity, empty bed contact time, molecular diffusion, and relative concentration.

Characterization of Organic Chemical Leaching From Resins During Cleanup/Preparation

The need to clean contaminants from XAD resins prior to use as an organic sorbent is well established (B-1,2). Impurities in XAD-2 and XAD-4 were characterized by Hunt et al (B-14, B-15), and Melton (B-16) using GC/MS. Reasons for concern about possible organic interferences from resins, especially XAD-2, were stated by Bean et al (B-17) who after soxhlet extraction with three different solvents, found aromatic hydrocarbons in many samples. Contaminants were found in the uncleaned resin, but not when a cleaned resin column was extracted for a system blank. This phenomena was also seen after the resin was used in distilled water by Care et al (B-18). The occurence of contaminants was observed in the blanks and samples of this project. The explanation of Bean et al (B-17) is that during the sampling of water, the XAD resin fractures under the back-pressures produced and the hydrocarbons are released. Another possible reason may come from the alternating expansion of the resin during sampling and subsequent contraction after ether elution and storage under methanol.

Breakthrough of Organics Sampled by MRR Accumulators

Harris, et al (B-19) pointed out that flow rate is not as important as measuring the velocity of water through a resin column in understanding mass transfer. Measuring linear velocity (cm/min) allows for column diameter, and therefore, the mechanics of mass transfer. Following this logic there are two types of resin capacity limitations: The first is intrinsic weight capacity (k'). This is exceeded by saturating all of the available adsorption sites due to high organic loadings. This capacity is measured by performing isotherms with the resin and the compound of interest.

Volumetric capacity is the second type of limitation. This capacity is determined from the partitioning of the compound between the adsorbent and solvent, as in a chromatographic process. In volumetric capacity, compounds adsorbed at the top of the column are swept out after a certain volume of water has passed through. This phenomena causes breakthrough at loading significantly below the intrinsic weight capacity of the resin in a column sampler. According to Harris et al (B-19), volumetric capacity is limiting at compound concentrations less than or equal to 100 ppm. When this process is occurring, breakthrough is independent of concentration.

The Effect of TOC on The Adsorption of Trace Organics by Macroreticular Resins

TOC, or humic material, in a water sample strongly influences the overall performance of a macroreticular resin sampler for composite water sampling of organic micropollutants. TOC has a concentration 1000 times greater than the compounds being investigated in this study.

The reliability of literature procedures is questioned for the purpose of isolating trace organics from large volumes of water over long period of time. Comparison of the various sampling systems from the literature is difficult because of the variety of sampling conditions used. It was the purpose of this project to develop quality assurance data on the resin samplers. Specifically, it was important to gain an understanding of adsorption capacity and the factors which effect these phenomena.

EXPERIMENTAL

The cleaning procedure outlined by Junk et al (B-1) of new macroreticular resin was used in this project. The two types of resin (XAD-2 and XAD-8) were soxhlet extracted for 24 hours each by methanol, acetronitrile and ethyl ether, respectively. Approximately 700 mL of each resin was extracted with 850-900 mL of solvent. The solvent distillation rate in the soxhlet was about 30 mL/min. During each soxhlet step, a blank and waste solvent sample were taken and analyzed by capillary gas chromatography. Qualitative analysis was needed to characterize the classes of organic compounds removed during solvent washing. GC/MS analysis was completed to characterize the major contaminants.

After the sample elution, evaporative concentration and capillary gas chromatographic analysis was performed in the same way that the pilot plant samplers were processed. Qualitative (peak retention time) and semiquantitative (peak response) comparisons are made.

Breakthrough of organics from the MRR accumulators was suspected, although the degree to which this occurred and the classes of compounds breaking through was unknown. Breakthrough is a function of the number of bed volumes of water processed by the resin. The combined XAD-2/XAD-8 resin beds in the samplers have a volume of approximately 200 mL. Water flowed through the bed at approximately 35 mL/min for 3 days, for a total number of bed volumes of 700. The experimental design of the breakthrough columns was identical to the method used for the samplers. The use of breakthrough columns to check the samplers is a necessity in a good quality assurance study. New resin samplers were prepared for the breakthrough columns.

Field Sampling Set-up

Processed Delaware River Water from the pilot plant after the ozonation process was used for this project, location O_3(PP). The Delaware River was subjected to conventional water treatment processes excluding chlorination (i.e. sedimentation, flocculation, coagulation, and rapid sand filtration). The water was then ozonated. Water for this project was taken after ozonation detention tank (dose ≅ 1.2 mg/L, 30 minutes detention time) at sampling point 15-D in the pilot plant.

For the first sampling run, a 1/4 inch teflon line was drawn from the water source. An 1/8 inch Teflon line was run into the 1/4 inch line from a 40 liter reagent feed bottle. This bottle contained 10% H_3PO_4 and 10% Na_2SO_3 (by weight). The pH of the sample was adjusted to fall between 2.9 and 3.5. The 1/4 inch influent line was split into 6-1/8 inch Teflon lines. 5 of these lines were fed into resin sampler. A 6th, 1/8 inch influent line with a flow controller was used to feed a composite water sampler. The resin samplers had been previously used in the monitoring studies at Torresdale. Each of the 5 samplers consisted of a glass column (750 mm X 50 mm ID) with a glass frit and a Teflon stopcock at the bottom. The 1/8 inch influent lines fit into a Teflon flow controller at the top of each sampler. This design allowed the samplers to be closed and pressurized to approximately 20 psi.

Breakthrough samplers were connected to the bottom of three of the main samplers. Each breakthrough sampler consisted of 3 Teflon column sections giving overall column dimensions of approximately 600 mm long X 45 mm ID. A 1/4 inch plastic line leading to a central Cole-Palmer Masterflex pump was placed at the effluent end of each sampling setup. The pump was adjusted to draw approximately 35 mL/min through each sampler.

Run No. 2 was carried out under somewhat different conditions. The glass covers, with Teflon flow controllers, were removed from the samplers. A glass tube section was added with an arm piece to drain off overflow water. This design change left the system open and therefore at atmospheric pressure. Reagent feed water was added for the entire 70 hour run. All other run conditions were identical to Run No. 1. Tables B-2 and B-3 show the water quality and flow data for runs 1 and 2.

Ether Elution and Concentration

After a 70 hour sampling run, the water was drained off the columns. The resin was then extracted with ether in 3 elutions of 150, 100, and 100 mL, respectively. The 3 aliquots of ether were combined and stored (below 0°C to freeze out water) until the concentration step. 350 mL of ether was passed through approximately 30 mL of sodium sulfate in a 5 cm diameter column to remove residual water. The samples were then evaporated to 10 mL using a Kuderna-Danish (K-D) apparatus. A micro K-D system was subsequently used to concentrate the sample under a nitrogen stream to 1 mL. Table B-4 outlines the procedure for using macroreticular resin samplers including setup, extraction, and cleaning of samplers.

After Kuderna-Danish concentration, quality assurance samples were spiked with n-alkane hydrocarbon standards. The n-alkane range was C_8 through C_{26} without C_{24}. The alkane concentration in the 1 mL concentrated sample were 20 ug/mL except C_{21}, C_{23}, C_{25}, and C_{26} which were 10 ug/mL. Two main reasons for the use of internal standards in this project were: (1) to normalize quantification and (2) to determine the column resolution

TABLE B-2. WATER QUALITY PARAMETERS FOR RUNS 1 AND 2 AT O_3(PP)

Parameter	Run 1 10/1/81		Run 2 3/3/81	
	Value	Date	Value	Date
pH (adjusted)	3.2	(10/1)	3.3	(3/3)
	8.0	(10/3)[a]	3.4	(3/4)
			3.25	(3/6)
TOC (ppm)	1.91	(9/29)	1.83	(3/3)
	1.51	(10/6)	1.96	(3/9)
			1.79	(3/10)
O_3 utilized (ppm)	1.65	(9/29)	0.76	(3/5)
	1.82	(10/6)	0.63	(3/9)
O_3 residual (ppm)	0.00	(9/29)	0.01	(3/5)
	0.03	(10/3)	0.00	(3/9)

[a] 20 hrs. into Run 1, the reagent feed water (10% H_3PO_4 and 10% Na_2SO_3) was no longer added to the inlet line. The pH for the remainder of the run was approximately 8. The run lasted 70 hours.

TABLE B-3: SAMPLER FLOW RATES AND TOTAL VOLUMES FOR RUN 1 AND 2 AT O_3(PP)

	Run 1 10/1/81 Flow Rate (mL/min)			Total Volume	Run 2 3/3/81 Flow Rate (mL/min)			Total Volume
Sampler	10/1	10/2	10/3	(Liters)	3/3	3/4	3/6	(Liters)
16/1	36	33	37	152	36	36	34	152
15/2[a]	37	35	34	156	38	34	34	152
19/3	37	36	35	154	37	35	35	152
21/4	36	34	35	150	36	34	35	150
14/5	32	33	33	131	36	34	35	150

[a] Sampler 15/2 ran for 1 hour extra at 70 mLs/min.

efficiency, as seen by the peak shape of the standards, and (3) normalize retention time into Kovats Indices.

Table B-4: EXPERIMENTAL DESIGN - QUALITY ASSURANCE PROGRAM

I. Complete a series of studies simultaneously

A. Operate 5 MRR extractors in parallel at standard conditions of flow rate (2.1 L/hr) for 70 hours (147 L) at pH 2-4. Use an analagous sampler after 3 regular ones to check breakthrough.

B. Elute Sampler

1. Elute the resin samplers before running and clean the column (column blank)
2. Run sampler and elute with 150, 2 x 100 mL
3. Elute next 100 mL on two columns as elution efficiency check

C. Clean samplers

1. 200 mLs methanol
2. 2 x 100 mL 0.1 N NaOH
3. 2 x 200 mL distilled water
4. 150 mL methanol for storage

D. Analysis of samples

1. Analyze samples 1 - 3 by capillary column GC
2. Analyze breakthrough samples and breakthrough column blanks

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Gas Chromatography

The gas chromatograph used was a Carlo Erba 2150 with a split/splitless injector and a flame ionization detector. Conditions were as follows:

Temperature of injector and detector was 275°C.
Makeup gas for flame: 0.3 kp/cm^2 H_2 (prepurified) and 0.9 kp/cm^2 Air (Zero Grade).

Septum purge on injector was 1-2 mL/min.

A 0.9 to 1.5 μL sample is pulled back into a 5 μl syringe. The needle is inserted into the injector with the splitter closed and held. The 5 second hot needle technique was used with a cool oven and the oven door open. After 5 seconds, the syringe is withdrawn from the injector. At 20 seconds, the oven door is closed and the temperature program is started (B-21). After 45 seconds the splitter is opened. The temperature program used was 50°C to 250°C at 3.5°C per minute with a 3 minute hold at 50°C and a 15 minute hold at 250°C.

Chromatography columns differed for the two runs. Run No. 1 used a 30 meter x 0.33 mm ID, SE-30, glass capillary column. A 60 meter X 0.33 mm. ID, SE-30 fused silica capillary column was utilized for the second run. The carrier gas for all gas chromatography was hydrogen. The linear velocity was determined by methane gas retention time being approximately 0.5 meters/second.

RESULTS

1) Resin Cleanup

Soxhlet extraction for 24 hours with methanol, acetonitrile and ether, followed by a 0.1N NaOH, was found not to clean the resin adequately (See Figure B-2). The criteria to judge the cleaning procedure of the sampler was defined by the relative number of GC peaks and their response when comparing chromatograms. The cause of the GC peaks observed is thought to be due to leaching of residues not extracted from pores in the resin during the soxhlet process. The cleanup procedure was completed by an additional step of alternately eluting with 200 mL of ether then 200 mL of methanol then 200 mL of ether which was concentrated to 1 mL for GC analysis. This was repeated until the ether elution had an acceptable low number of peaks on its chromatogram (See Figure B-2).

GC/MS analysis of the unconcentrated XAD-2 and XAD-8 soxhlet extractions are shown in Table B-5. The two different resins exhibit entirely different background contaminant matrices except for napthalene. Table B-6 shows many of the identifications on Table B-5 have been previously identified from XAD-2 resin. The XAD-8 resin artifacts have not been previously identified in the literature. Artifacts can limit the applicability of the resin data if these same compounds are found in the Delaware River water and/or as a result of a unit process under investigation in the Pilot and Torresdale Plant.

2) Ether Extraction Efficiency

After the mixed bed resin was eluted with 200 mL and 2 X 100 mL of ether, duplicate fourth elutions of the samplers showed few GC peaks. These results showed that 3 ether elutions were quite satisfactory in extracting the resin sampler beds. See Figure B-2.

3) Sample Reproducibility

Figure B-3 is a plot of the standard deviation of the retention time versus the carbon number of the internal standards for Run No. 1. The standard deviation can be seen to be low overall and level at the highest weight internal standards. The higher standard deviation for blanks compared to the samples is attributed to improvement in GC analysis technique. Solvent blanks, column blanks and samples were analyzed in successive order.

TABLE B-5: XAD RESIN CLEAN-UP: SOXHLET EXTRACTIONS - GC-MS TENTATIVE IDENTIFICATIONS

COMPOUNDS[b]	XAD-8[a]			XAD-2[a]		
	CH_3OH	$CH_3C{\equiv}N$	$(C_2H_5)_2O$	CH_3OH	$CH_3C{\equiv}N$	$(C_2H_5)_2O$
Toluene	X	X				
C6-Alcohol (e.g. 4-methyl-2-pentanol)	2					
C2-Benzene	3	3				
Benzaldehyde	X					
C4-Benzene	2	2				
C2-Styrene	4	2				
Divinyl Benzene	X					
Naphthalene	X					
Nitrooctanone	2			X	X	
1-Undecanol	X					
Diethyl Phthalate	X					
C-17 HC Branched	X					
Nonamide	X					
Dichlorobenzophenone	X					
N-(p-chlorophenyl)-4-chlorobenzamide	X					
Methyl Benzoate						
C2-Benzaldehyde				X		
C2-Acetophenone				X		
Methyl Naphthalene				X		
Biphenyl				2		
C2-Naphthalene				X		
Methyl Styrene				X		
Methacrylic Acid	X				3	

Ethyl Acetate is a solvent impurity of ether

a) 900mL Solvent/700mL resin successively extracted with CH_3OH, $CH_3C{\equiv}N$, $(C_2H_5)_2O$ - 24 hour Soxhlet each. A sample was injected directly into the GC/MS.

b) Tentative identification-No retention time data has yet been correlated. Identification completed by MS only.

Table B-6: XAD RESIN CONTAMINANTS IDENTIFIED

Compound	Resin Cleanup XAD-2 Blank (Drexel)[a,f]	XAD-2 Solvent Elutions: Ether[b] ug/5.5g resin	XAD-2 Solvent Elutions: Ether[c] Relative amt.(range)	XAD-2 Solvent Elutions: CH_2Cl_2[d] µg/g of resin	XAD-2 Thermal Elution[e]	Resin Clean-up XAD-8 Blank (Drexel)[a,f]
Undecane		23-39				
Toluene		0 to 9				X
C2-Benzene		0.9-3.2	890-5600			
C3-Benzene		0.4-1.3	150- 420			
C4-Benzene			720-1820	102		X
C5-Benzene			70-1000			
C6-Benzene			X	X		
Styrene		1.3-5.9	690	19		
Methyl indan			180-3040			
Methyl styrene	X		X			
C2-Styrene			400-5160	15-320	X	X
C3-Styrene					X	
Dimethyl indan			450			
Tetralin			360			
Divinyl benzene			630-790	45		X
2-Pentenyl benzene			240			
1,1A,6,6A-Tetrahydro-cycloprop-A-indene			170			
Methyl benzoate	X		1720		X	
Acetophenone			90			
C2-benzaldehyde	X		120			
Naphthalene	X		1390	470	X	X
C2-Methyl benzoate			50			
C2-Acetophenone	X		50			
Methyl naphthalene is.	X		40-70	X		
Methyl indene				67		
C2-naphthalene	X			X		
Biphenyl	X			69		
Methyl biphenyl				X		
C2-Biphenyl				X		

Table B-6: XAD RESIN CONTAMINANTS IDENTIFIED (CONT'D)

Compound	Resin Cleanup XAD-2 Blank (Drexel)[a,f]	XAD-2 Solvent Elutions			XAD-2 Thermal Elution[e]	Resin Clean-up XAD-8 Blank (Drexel)[a,f]
		Ether[b] ug/5.5g resin	Ether[c] Relative amt.(range)	CH_2Cl_2[d] µg/g of resin		
1,1'-Methylene-bis-benzene						
1,1'-Ethylidene-bis-benzene				X		
1,1'-(1,2-ethenediyl) bis-benzene				130		
1,1 -bis(p-ethylphenyl) ethane				X		
Benzoic acid				26		
					X	

a) 900 mL solvent/700 mL resin succesively extracted with CH_3OH, $CH_3C\equiv N$, $(C_2H_5)_2O$-24 hour soxhlet each. See Table B-5. All identifications are tentative.

b) Cleaned resin (15 mL methanol slurry (5.5 g dry resin)) eluted with 2 bed volumes of ethyl ether.
Care, R., Morrison, J.D., Smith, J.F., "On the Limits of Detection of Traces of Volatile Organics in Water Using Amberlite XAD-2 Resin", Water Res.; 16, 663, (1982).

c) Cleaned resin eluted with ether.
Melton, R. et. al. "Comparison of Grob Closed-Loop-Stripping Apparatus (CLSA) to other Trace Organic Methods" in Keith, L. "Advances in the Identification and Analysis of Organic Pollutants in Water." Volume 2, (1981) Chapter 36. Ann Arbor Science Publ., Ann Arbor, Mich.

d) Cleanedup XAD-2 Resin eluted with CH_2Cl_2.
Hunt G. and Pagano N., "Potential Contamination from the Use of Synthetic Adsorbents in Air Sampling Procedures," Analytical Chemistry, 54, 369, (1982).

e) Lochmuller, C. H. and Jensen, E. C., "XAD-2 Thermal Blank Determination", EPA 600/82-8-047 (1981).

f) Additional compounds found only in XAD-8 resin cleanup: Toluene, C-6 alcohol, benzaldehyde, nitrooctanone, isomers, undecanol, diethyl phthalate, C17 HC-branched, nonamide, dichlorobenzophenone, N-(p-chlorophenyl)-4-chlorobenzamide, methacrylic acid. See Table B-5. All identifications are tentative.

GC capillary column performance was evaluated by running a test mixture on the column (B-20). Analysis of column testing showed very little degradation for the 30 meter SE-30 glass column used in Run 1. Run 2 utilized a 60 meter SE-30 fused silica column. Two-thirds through the analysis of Run 2 samples, "tailing" was observed in the 3 methyl esters in the test mixture. Breaking off a small length of column of the injector end and then flushing the column with solvent decreased the tailing satisfactorily. Comparison of n-alkane internal standard peak areas showed no significant change in column performance.

Analytical Precision

Table B-7 A and B represents the precision (reproducibility) when all the sample analysis steps are included. GC chromatographic peaks were arbitrarily selected by a Kovats number ± one Kovats unit, from each Kovats window for 5 replicate samples. Peak areas were normalized to an internal standard (C-21). The mean ($\bar{x}$), standard deviation (σ) and relative standard deviation ($\sigma/\bar{x}$) were computed and compared.

Of the two tests, the relative standard deviation is more important to consider than the standard deviation because peak response change is in sensitivity rather than a lower limit of detection. The standard deviation represents the y-intercept of a standard curve, but of more concern is the slope of the curve or detector response sensitivity represented by the relative standard deviation.

Sample analysis contains a number of steps all of which can affect the variability of the concentration measurement of a sample:

E_1 Sampling differences f(flow rate, organic loading)
E_2 Ether elution of resin bed f(technique, volume, elution time)
E_3 Kuderna-Danish concentration f(evaporation rate, contamination, temperature, N_2, flowrate)
E_4 Addition of internal standard f(amount added)
E_5 Gas chromatography f(conditions, injection size, column phase integrity).

These steps in a precision model are considered additive such that each step contributed a portion of the total variability.

$$E_t = E_1 + E_2 + E_3 + E_4 + E_5.$$

Each step should be considered when attempting to measure precision of analysis between replicable samples.

Tables B-7 shows the precision of the measurement of internal alkane standards between 5 replicate samples of arbitrarily selected peaks (one for each Kovats Index Window). The peak areas of the standards were normalized to the C-21 alkane standard. Calculations of the internal standards deviation and relative standard deviation were made. These data show the largest errors in the sampling ether elution and concentration steps (E_1, E2 and E_3) and in the addition of internal standards and gas chromatography (E_4 and

TABLE B-7. REPRODUCIBILITY STUDY: ARBITRARILY SELECTED SAMPLE PEAKS FROM KOVATS INDICES WINDOWS FROM RUN NO. 1

KI Window	Normalized Area (Mean)	Standard Deviation	Relative Standard Deviation
800-900	0.251	0.293	0.116
900-1000	0.133	0.028	0.211
1000-1100	0.164	0.061	0.374
1100-1200	0.275	0.099	0.360
1200-1300	0.703	0.215	0.306
1300-1400	0.176	0.020	0.114
1400-1500	0.078	0.022	0.276
1500-1600	0.049	0.024	0.483
1600-1700	0.051	0.007	0.137
1700-1800	0.678	0.327	0.482
1800-1900	0.026	0.003	0.335
1900-2000	0.173	0.047	0.272
2000-2100	0.741	0.044	0.060
2100-2200	0.057	0.029	0.508
2200-2300	0.047	0.015	0.314
2300-2400	0.008	0.007	0.214
2400-2500	0.041	0.005	0.114
2500-2600	0.035	0.007	0.208
Mean	---	0.054	0.271

Normalized to C_n=21 Internal Alkane Standard $\frac{(\text{Area } C_n)}{(\text{Area } C_{21})}$

TABLE B-8. REPRODUCIBILITY STUDY: INTERNAL ALKANE STANDARDS

KI Window	Normalized Area (Mean)	Standard Deviation	Relative Standard Deviation
800-900	2.909	0.274	0.094
900-1000	3.261	0.296	0.091
1000-1100	4.384	0.896	0.204
1100-1200	5.166	0.341	0.066
1200-1300	3.155	0.275	0.087
1300-1400	2.868	0.260	0.091
1400-1500	2.854	0.177	0.062
1500-1600	2.707	0.138	0.051
1600-1700	2.831	0.317	0.112
1700-1800	2.348	0.205	0.087
1800-1900	2.141	0.096	0.045
1900-2000	2.023	0.082	0.040
2000-2100	1.965	0.076	0.039
2100-2200	---	---	---
2200-2300	1.743	0.052	0.030
2300-2400	0.778	0.230	0.030
2400-2500	1.009	0.124	0.123
2500-2600	0.761	0.036	0.048
Mean	---	0.204	0.072

Normalized to C_n=21 Internal Alkane Standard $\frac{(\text{Area } C_n)}{(\text{Area } C_{21})}$

E_5). The average of all the relative standard deviations calculated was E_T = 27.1%. This is an estimate of the total sample variability. This includes the relative standard deviation associated with the addition of internal standards and gas chromatography (E_4+E_5) which was shown in Table B-8 to be 7.2%, which is the mean relative standard deviation for all the internal standards.

The above analysis shows that the 95% confidence interval for relative peak response to C-21 has a multiplicative factor of 2.6. This value was used to determine the peak response ranges shown in the peak distribution tables (e.g. Table B-9). This table supplies the data for which the Chi-square test was performed. Figure B-4 and B-5 are chromatographic plots of the reproducibility study and breakthrough study, respectively.

5) Resin Sampler Breakthrough

Figure B-6 shows a chromatographic plot of a typical sample, breakthrough sample and blank. Linear volocity through the bed has been shown to be an important parameter affecting organic breakthrough on XAD-2 resin (B-18). Using the equation L = F/r, the flow, F = 35 mLs/min and the radius of the sampler, r = 2.5 cm, the approximate linear velocity (L) for this study is 1.8 cm/min. Harris (B-18) indicates that if the linear velocity is below 3.0 cm/min the breakthrough curve for resin is independent of flow rate. The study carried out by Harris (B-18) was done considering only one compound at a time, therefore, no competition was present to affect volumetric capacity of the resin. In this study, competition maybe an important consideration, possibly lowering the linear velocity below which breakthrough is independent of flow rate.

Breakthrough analysis of Runs 1 and 2 included using the Chi-square test to compare peak populations for normal and breakthrough samples. Observed and expected data was split into 6 peak response ranges and 4 Kovats Index ranges. (See Table B-9). The null hypothesis for the Chi-square test of both runs was to see if peak populations from the normal and breakthrough samples were homogeneous i.e. did complete breakthrough occur for the run? Tables B-10 and 11 present the results of the Chi-square tests for Runs 1 and 2. The test for Run 2 shows the null hypothesis to be true; the peak populations are homogeneous so complete breakthrough seems to have occurred. Chi-squares for the Run 1 comparison rejects the null hypothesis, that the two samples did not come from one homogeneous population. Further Chi-square analysis of Run 1 determined the major deviations between the normal and breakthrough samples occurred in the following categories; the peak response range 0.03 to 0.1 (represents 0.9 to 6 ppt equivalent concentration) and over the Kovats Index range 800-1100, Table B-10.

From the above statistical analysis, the breakthrough appears to be related to weight capacity limitations, due to the Total Organic Carbon (TOC) of the influent water (2 mg/L) and large volumes of water through the resin (~150 L).

Thurman et al (B-11) calculated capacity factor values (log k') for organic compounds on XAD-2 and XAD-8. Aiken et al (B-10) studied capacity of XAD-2 and XAD-8 for fulvic acid and other organic compounds using South

Table B-10 (CHI)^2 Analysis of the October 1-4, 1980 (QA1) Sample and Breakthrough Peak Distributions

		Peak Response						
Kovats Range		0.01 to 0.03	.031 to 0.10	0.1 to 0.31	0.31 to 1.0	1.0 to 3.16	3.16 to 31.6	#peaks
800-1000								
Sample	observed expected	4.2 (13.02)	9.6 (22.66)	22.2 (13.75)	20.6 (7.33)	4 (5.13)	28 (1.57)	63.4
Breakthrough	observed expected	7.5 (11.5)	18 (20.02)	18 (12.15)	5.5 (6.4)	2.5 (4.53)	4.5 (1.38)	56
1100-1400								
Sample	observed expected	5.2 (14.13)	18.6 (24.59)	25 (14.93)	14.2 (7.96)	4.2 (5.56)	1.6 (1.7)	68.8
Breakthrough	observed expected	11.5 (10.68)	19 (18.59)	12 (11.38)	3.5 (6.0)	5.0 (4.21)	1.0 (1.29)	52.0
1400-2000								
Sample	observed expected	18.0 (18.44)	39.2 (32.1)	18 (19.48)	4.4 (10.38)	8.8 (7.26)	1.4 (2.22)	89.8
Breakthrough	observed expected	24 (13.86)	20.5 (24.13)	9 (14.64)	6.5 (7.8)	6.5 (5.46)	1.0 (1.66)	67.5
2000-2600								
Sample	observed expected	24.4 (16.72)	37 (29.27)	5 (17.8)	6.5 (9.47)	8.5 (6.62)	0.5* (2.02)	81.9
Breakthrough	observed expected	15.5 (11.92)	30 (20.91)	7.5 (12.69)	1 (6.76)	4 (4.73)	0.5* (1.446)	58.5
# Peaks		110.3	191.9	116.7	62.2	43.5	13.3	537.9

Degrees of Freedom: 7(5)=35

Critical value of $\chi^2_{(0.05)}$= 49.88

Calculated χ^2 value = 124.15

* True observed value was zero but .5 arbitrarily substituted

Ho: The two populations are Homogeneous

- Reject Ho -

Table B-11 (CHI)^2 Analysis of the March 3-7, 1981 (QA2) Sample and Breakthrough Peak Distributions

		Peak Response						
Kovats Range		0.01 to 0.3	0.3 to 0.1	0.1 to 0.31	0.31 to 1.0	1.0 to 3.16	3.16 to 31.6	# peaks
800-1100								
Sample	observed	6.2	25	28	10.4	2.4	3	75
	expected	(13.38)	(27.4)	(20.6)	(5.8)	(3.94)	(3.78)	
Breakthrough	observed	7.5	15	12	1.5	2.5	6	44.5
	expected	(7.94)	(16.25)	(12.2)	(3.47)	(2.35)	(2.24)	
1100 - 1400								
Sample	observed	13	31.4	19.6	3.6	1.2	1.8	70.6
	expected	(12.60)	(25.79)	(19.4)	(5.5)	(3.73)	(3.55)	
Breakthrough	observed	11	11.5	11.5	1.5	2	3.5	41
	expected	(7.31)	(14.98)	(11.3)	(3.2)	(2.16)	(2.06)	
1400-2000								
Sample	observed	17.6	30.8	20.8	6.8	3.2	1.0	80.2
	expected	(14.31)	(29.8)	(22.07)	(6.25)	(4.23)	(4.04)	
Breakthrough	observed	8.5	15	15	4	3	4.04	50
	expected	(8.92)	(18.26)	(13.76)	(3.9)	(2.64)	(2.52)	
2000-2600								
Sample	observed	7.4	15.2	4.8	2.4	4.0	0.5*	34.3
	expected	(6.12)	(12.53)	(9.44)	(2.67)	(1.8)	(1.73)	
Breakthrough	observed	2.5	7	2	2	3.5	0.5*	17.5
	expected	(3.12)	(6.39)	(4.82)	(1.36)	(0.92)	(0.88)	
# Peaks		73.7	150.9	113.7	32.2	21.8	20.8	413.1

Degrees of freedom 7(5)=35

Critical value of $x^2_{(0.05)}$= 49.88 Calculated x^2 value = 45.96

* True observed value was zero but .5 arbitrarily substituted

Ho: The two populations are Homogeneous

- Accept Ho -

TABLE B-12. CALCULATED AND ACTUAL CAPACITY FACTORS FOR SPECIFIC ORGANIC COMPOUNDS ON XAD-2 AND XAD-8.*

	XAD-2		XAD-8	
Compounds	k'		k'	
pentanoic acid	214	(327)	125	(184)
hexanoic acid	766	(1336)	377	(651)
heptanoic acid	1995	(2500)	960	(1745)
benzoic acid	471	(532), (830)	488	(601), (843)
p-toluic acid	1820	(3513)	1037	(2110)
valeric acid		(274)		(154)
phenol		(139), (151)		(325), (386)
caproic acid		(989)		(478)
aniline		(200)		(159)
benzaldehyde		(983)		(429)
benzene			452	
phthalic acid			144	
toluene			1406	

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* All data are calculated from reference B-10 to B-12.
A ( ) represents actual data from these references.

Platte River Water. The calculated and actual values for specific organic compounds are compiled in Table B-12. The equation below represents the capacity factor

$$k' = \text{Capacity factor} = \frac{\text{mass of solute on resin}}{\text{mass of solute in water phase}}$$

A calculated capacity factor can be substituted into

$$V_e = V_o\ (1+k')$$

where V_e is the breakthrough volume at 50% of influent concentration and V_o is the void volume (0.65 X bed volume). The equation will yield the breakthrough volume; where the effluent concentration is 50 percent of the influent concentration.

Aiken and coworker (B-10) gave an estimated capacity factor range of 50-100 for humic substances. Leenheer (B-8) studied a fractionation procedure for dissolved organic carbon (DOC) of the South Platte River. The DOC was measured to be 7.5 mg/L and its respective k' value was 43. In calculating the breakthrough volume for DOC in this study, k' values of 43 and 100 were used. It was assumed that the capacity factor of DOC from the Delaware River lies between that of the South Platte River and the upper limit of Aiken et al data (B-10). Equation; $V_e = V_o(1 + k')$ was used. Table B-13 shows calculated breakthrough volumes (using a resin bed volume of 200 mL) from the equation used to predict the breakthrough volume.

TABLE B-13. BREAKTHROUGH VOLUMES FOR DOC IN THE DELAWARE RIVER

Capacity Factor (k')	Void Volume (V_o) (V = 0.65 x bed volume)	Breakthrough Volume (V_e)
43	0.13	5.72
100	0.13	13.13

Assuming the larger k' value for Delaware River DOC of 100, a breakthrough volume of only 13 liters is calculated. After this volume, the DOC of the influent and effluent of the remaining 140 liters, run through the sampler resin beds, are approaching the same concentration. Therefore, it can be assumed that DOC can occupy a significant number of adsorption sites. Adsorption by other organic compounds in the sample water can be affected not only by less available sites, but also by competition with DOC. This idea is supported by similar evidence shown by Aiken et al (B-10). Their research showed that the pores of XAD-2 became "clogged" by "natural polyelectrolytes" resulting in a "low retentive capacitive" for those substances. It was stated that the "clogging" tended to decrease the resin capacity for smaller lower molecular weight organic compounds.

5) Base Extraction

Base extraction has been found to eliminate the observed chromatographic "hump" and improve peak resolution and detection. On the negative side, the procedure could remove compounds of interest or add contamination to samples. To study the effects, a Run 2 sample was chromatographed before and after base extraction. The detector response was plotted logarithmically, with the minimum response being 0.01 (0.6 ppt). Plots of the Run 2 sample before and after base extaction were utilized to observe significant changes in the number and response of peaks. Figure B-7 shows a profile comparsion of a Run 2 sample before and after base extraction. The comparison shows a significant fluctuation in the number and response of peaks after base extraction primarily for the small peaks below 0.01 relative response. The more concentrated GC peaks were not greatly affected base extraction. The decreasing response or loss of peaks does not appear due to the physical manipulation of the sample during the procedure. The more likely explanation is chemical in nature, perhaps the conversion to new compounds or the loss due to solubility changes, i.e. the DOC "hump" dissolving into the aqueous base solution. The increase or appearance of peaks have several possible explanations. Addition of contaminants by base during extraction is minimal, proven through blank ether extractions of the sodium hydroxide used in the procedure. The base could convert compounds accounting for some of the new peaks seen. Since it is known that the "hump" obscures the normal column baseline (as seen by an integrator) and peak detection, extraction may cause previously undetected or unintegrated compounds to be seen. Very polar substances cause the FID flame to be unstable when chromatographed on SE-30 stationary phase. This introduces noise which the integrator usually defines as a peak unless the sensitivity is decreased.

Subsequent GC-MS analysis identified (Table B-14) two types of organic compounds which undergo a significant decrease in concentration as a result of base extraction. The two are iso-propylidine sugars and di-ethyl and dibutyl (phthalates). The probable cause of the loss of these two materials is base hydrolysis. Thus, not only is there an acid-base titration but also base hydrolysis of compounds in the base extraction cleanup procedure.

V. Conclusions/Recommendations:

1) Cleanup/Preparation:

In the cleanup/preparation of the resin it would be advantageous to alternately rinse the resin with organic free water and ether to reduce the release of residual contaminants from the pores of the resin.

2) Ether Extraction Efficiency:

Three sequential elutions of 150, 100 and 100mL for the 200mL resin bed works satisfactorially.

3) Reproducibility:

After statistically reviewing the reproducibility (precision) data obtained from Run 1, it can be concluded that the retention times and peak areas of compounds from different samples can be compared. The estimated percent standard deviation for peak area, which is 27.2%, is large therefore small differences are probably system noise.

4) Breakthrough:

From the breakthrough results, it can be concluded that the total sample volume/resin volume was much too high. (~150 L/0.2 L, 700 bed volumes). Decreasing this ratio would reduce breakthrough.

Another recommendation concerning reduction of breakthrough deals with whether or not to acidify the sample water. When comparing runs 1 and 2 in this project, Run 1 has less breakthrough than Run 2. This was attributed to not acidifying the influent water after 20 hours into the run.

5) Base Extraction:

Base extraction, as a method for the cleaning of samples for GC analysis, has advantages and disadvantages. The procedure does remove high-molecular weight non-chromatographical compounds, but also removes base-hydrolyzable compounds of interest such as phthalates and iso-propylidine sugars.

TABLE B-14: SUMMARY OF TENTATIVE GC/MS IDENTIFICATIONS FOR REPRODUCIBILITY AND BREAKTHROUGH SAMPLES

Chlorinated	QA1 Column Blank	QA1 Sample	QA2 Sample (1)	QA2 Breakthrough Sample (1)	QA2 Sample (2)	QA2 Sample Base Extracted (2)
1. Chloroform			X	X		
2. Dichlorobromomethane	X		X	X	X	X
3. Dibromochloromethane		X		X	X	
4. Trichloroethylene			X			
5. 1,2-Dichloroethane				X		
6. Bis(2-chloroethyl)ether		X				
7. 1,2-Bis(2-chloroethoxy)ethane			X		X	X
8. Dichlorobenzene is.		X				
9. Tetrachloroethylene					X	X
10. 1,2-Dichloropropane						X
Aromatic						
1. Toluene	X		X	X	X	
2. C2-Benzene is.	3			3		
3. C3-Benzene is.	2	2		3		
4. Acetophenone	X	X	X	X		
5. Benzaldehyde			X	X		
6. C2-Benzaldehyde	2	1		2		
7. C2-Acetophenone	2			1		
8. Methyl benzoate(B)	X	X	X	X		
9. C2-Methyl benzoate(B)	2					
10. Naphthalene		X		X		
11. Benzene	X					
12. Styrene(B)	X					

TABLE B-14 (continued)

Miscellaneous	QA1 Column Blank	QA1 Sample	QA2 Sample (1)	QA2 Breakthrough Sample (1)	QA2 Sample (2)	QA2 Sample Base Extracted (2)
1. Ethyl Acetate(B)		X	X		X	X
2. C10 branched hydrocarbon		X			X	
3. 1,2;3,4-Di-O-isopropylidene-L-Arabinopyranose		X				
4. 1,2;3,5-Di-O-isopropylidene-D-Xylofuranose		X			X	
5. 2,3;4,6-Di-O-isopropylidene-L-Sorbofuranose		X		X	X	
6. 2,3;4,5-Di-O-isopropylidene-D-Fructopyranose		X				
7. Tributylphosphate		X				
8. Cyclohexane	X					
9. 3-Pentanone	X					
10. Methyl methacrylate(B)	X			X		
11. 2-Methyl-3-pentanone	X			X		
12. FAME			1	2		
13. 2-Ethyl-1-hexanol					X	X
14. Diethyl phthalate					X	
15. Dibutyl phthalate					X	
Tentative						
1. Methyl isopropyl ketone	X					
2. Ethyl sec-butyl ether	X					
3. Methyl isobutyrate	X					
4. 3-Methyl tetrahydrofuran	X					
5. Nitrooctanone(B)			X	X		
6. Benzothiazole		X				
7. Bis(2-chloroethoxy) methane		X				
8. Diphenyl ether		X				
9. Dichlorobenzaldehyde is.		1				
10. Methyl butanoate	X					
11. 3,4-Dimethyl tetrahydrofuran	X					
12. 2-n-Butyl tetrahydrofuran	X					
13. Di-Isoprpyl ketone	X					
14. 1,1-Diethoxyethane			X			
15. 1,1-Diethoxypropane			X			

NOTE: (B) GC/MS identified in resin cleanup solvent.

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LIST OF FIGURES

B-1 Schematic of Quality Assurance Experimental Design

B-2 GC Capillary Chromatographic Profiles of
- Resin Blanks - Solvent Blank (Bottle Blank)
- XAD-2 Clean-up - 900 mL, ether/700 mL Resin
- XAD-8 Clean-up - 900 mL, ether/700 mL Resin
- 4th Elution Solvent - 100 mL elutions after 150 mL, 2 x 10 mL

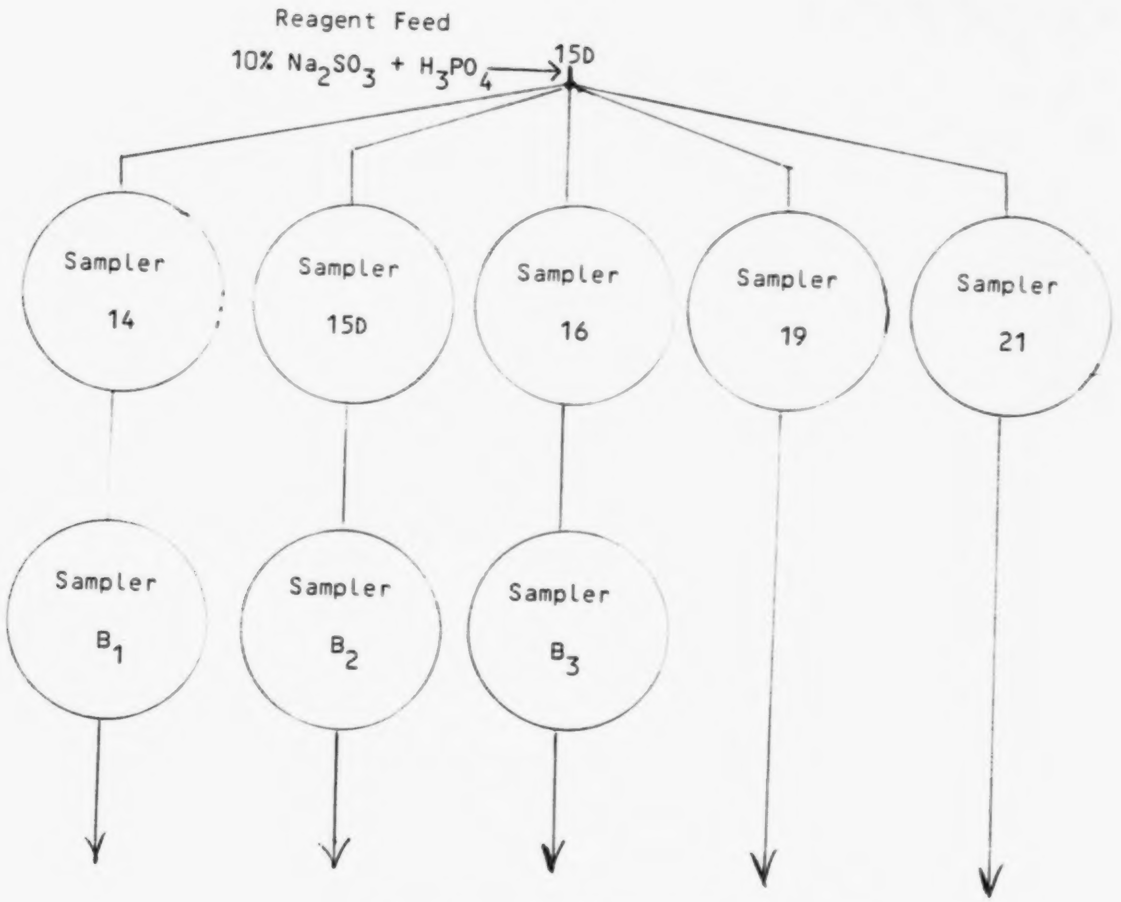
B-3 Retention Time Standard Deviation vs Carbon Number of Internal Standards for Quality Assurance Study

B-4 Reproducibility - Precision of Samples from Run 1 (QA1)

B-5 Reproducibility - Precision of Samples from Run 2 (QA2)

B-6 Breakthrough of Organics Adsorbed on XAD Resin Bed Samplers after 700 Bed Volumes

B-7 Effect of Base Extraction on GC Capillary Chromatographic Profiles


Reagent Feed
10% Na2SO3 + H3PO4
15D
Sampler 14
Sampler 15D
Sampler 16
Sampler 19
Sampler 21
Sampler B1
Sampler B2
Sampler B3

Pump Drawing 35 mls/min.

Each Sampler has a Mixed Bed of 100 mls each XAD-2 and XAD-8

Elution of Samplers with 150 ml 2 x 100 ml Aliquots Ether

Figure B-1 SCHEMATIC OF QUALITY ASSURANCE EXPERIMENTAL DESIGN

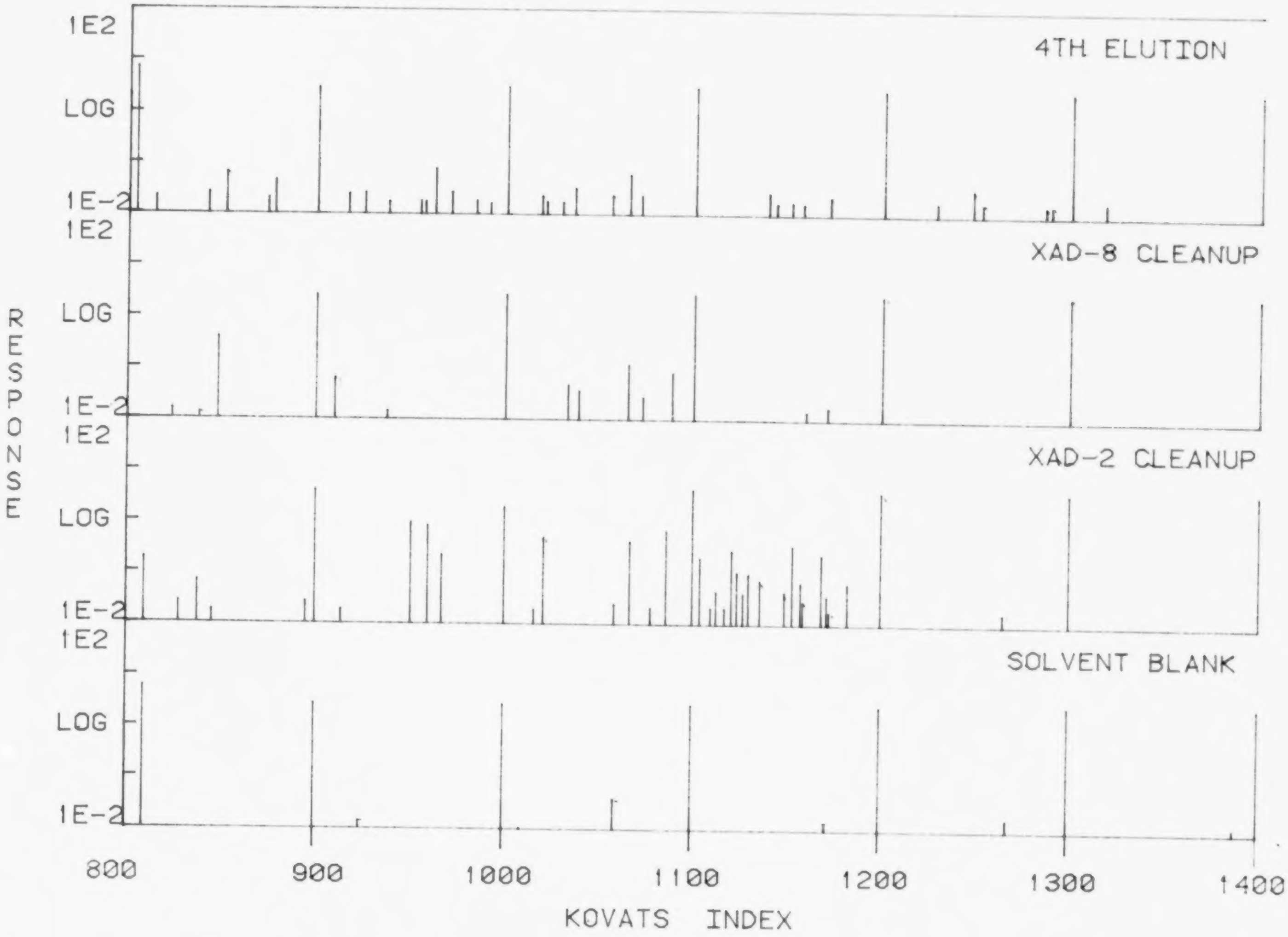


Figure B-2 GC CAPILLARY CHROMATOGRAPHIC PROFILES OF
- Resin Blanks - Solvent Blank (Bottle Blank)
- XAD-2 Clean-up - 900 mL, ether/700mL Resin
- XAD-8 Clean-up - 900 mL, ether/700mL Resin
- 4th Elution Solvent-100mL elutions after 150mL, 2 x 100 mL

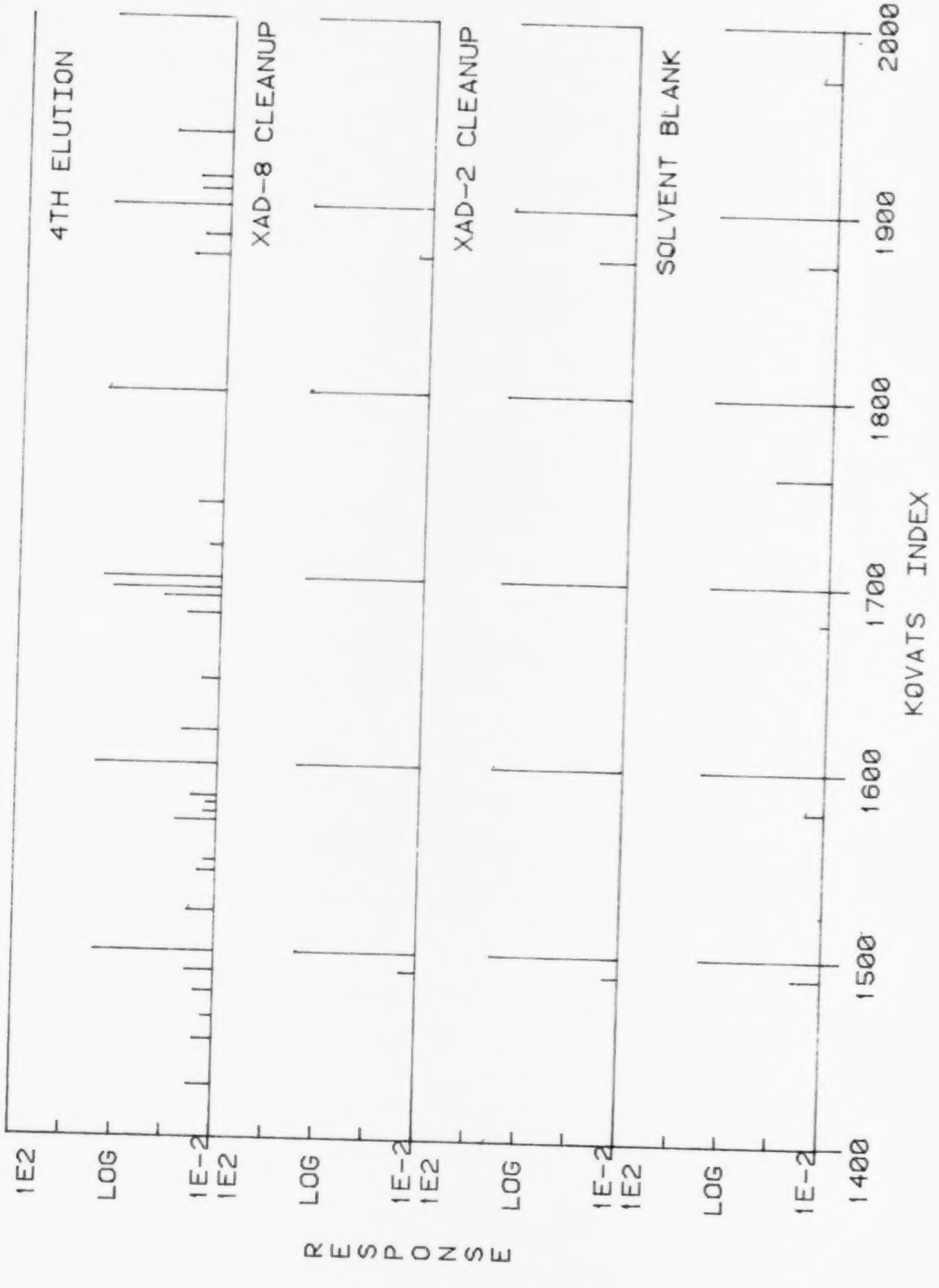


Figure B-2 (continued)

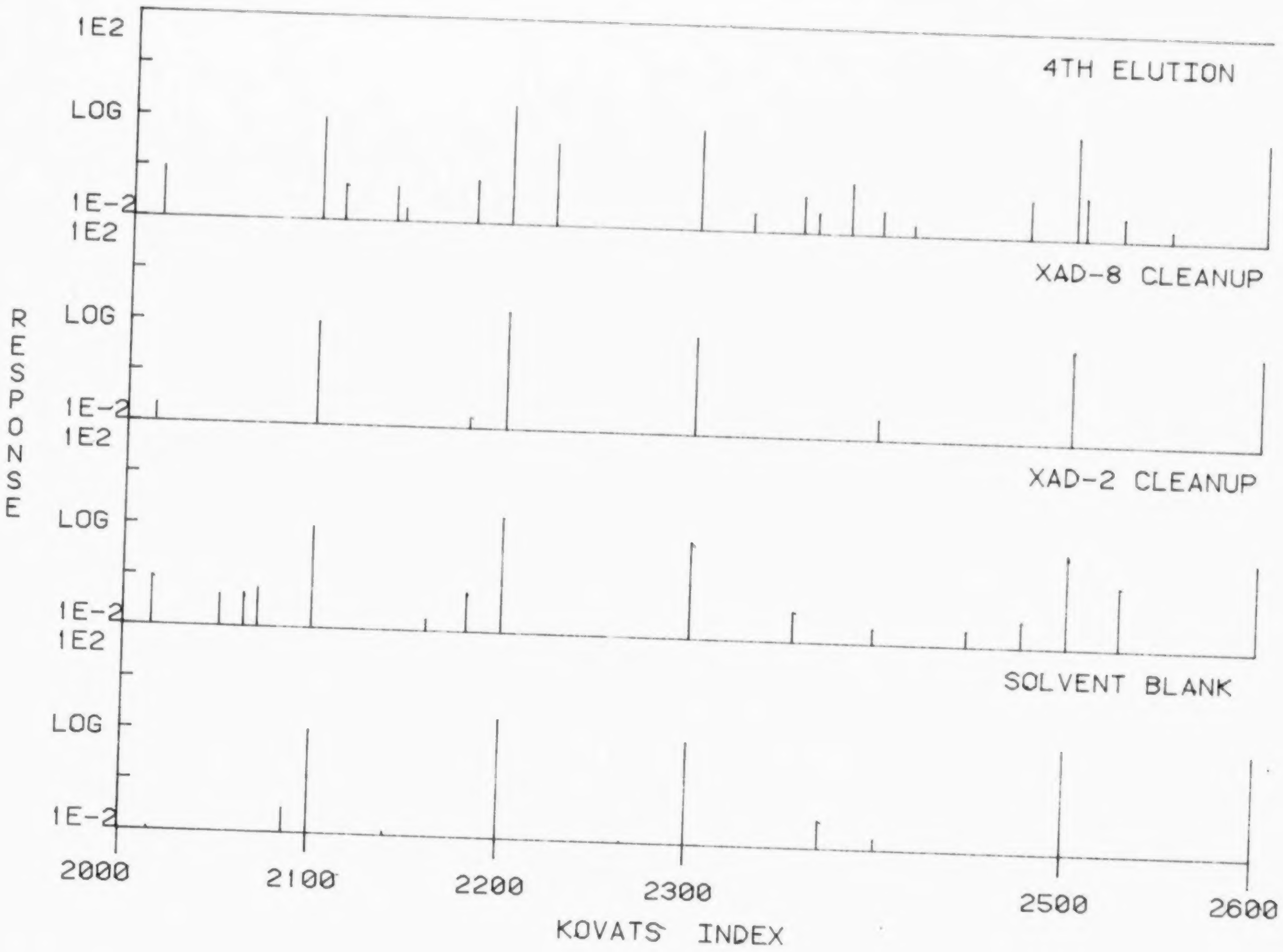


Figure B-2 (continued)

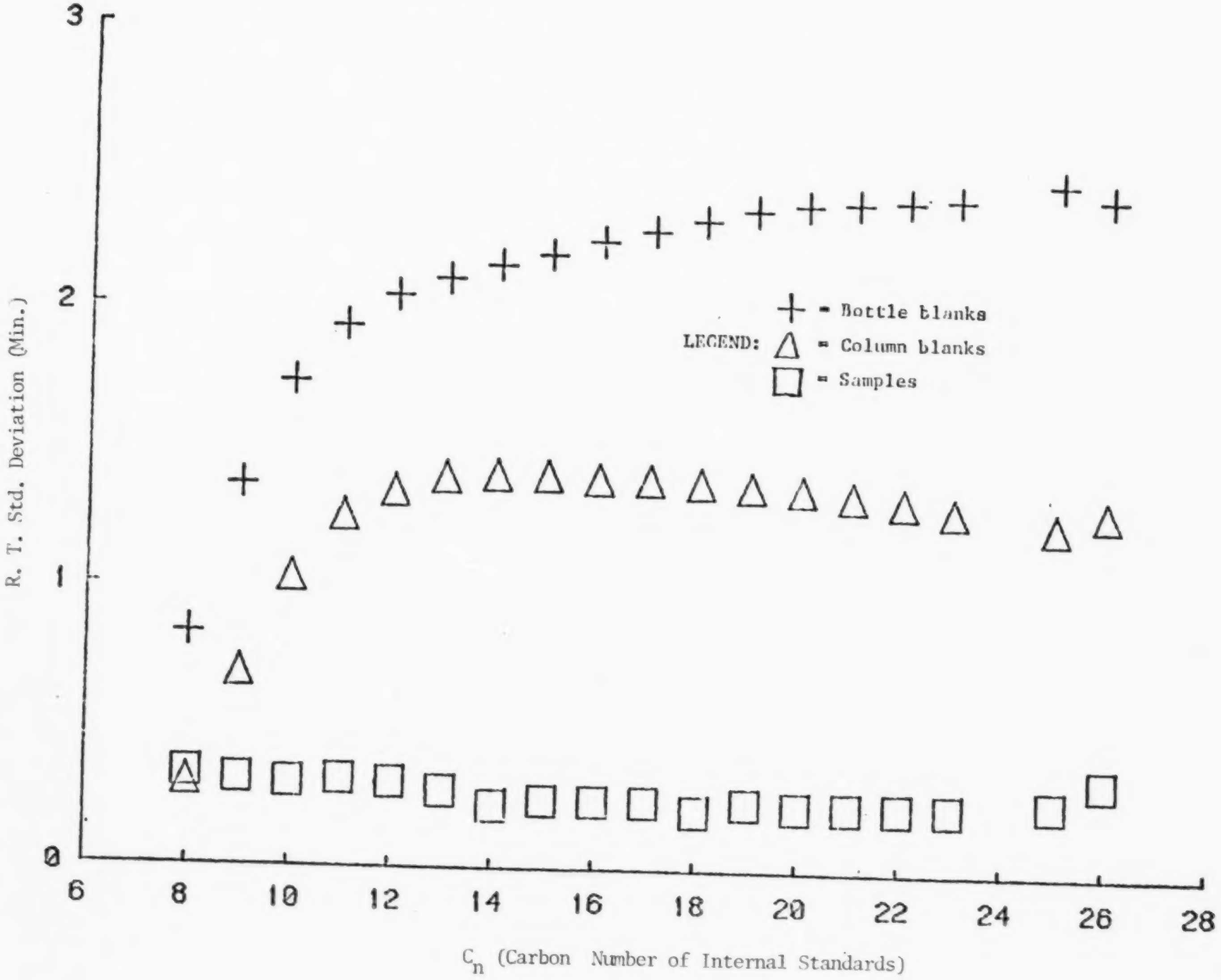


Figure B-3 RETENTION TIME STANDARD DEVIATION VS. CARBON NUMBER OF INTERNAL STANDARDS FOR QUALITY ASSURANCE STUDY

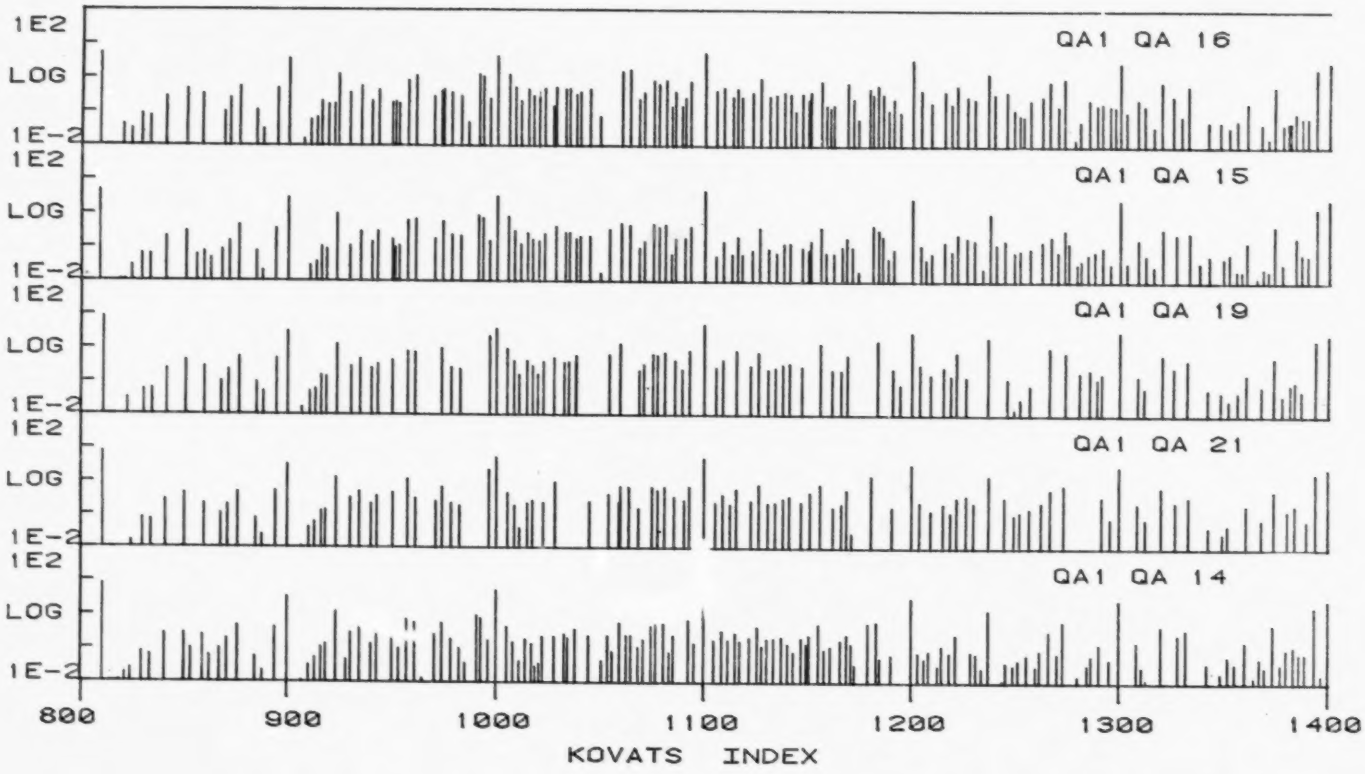
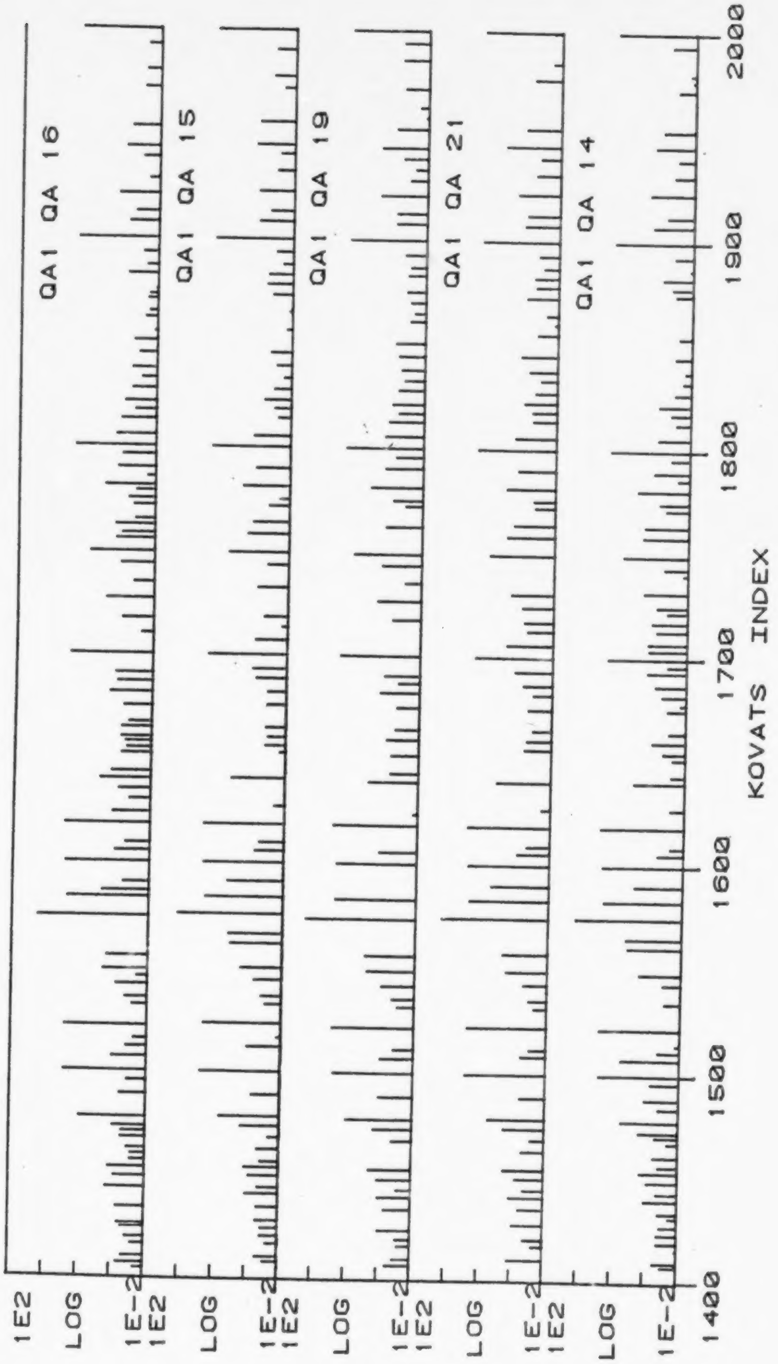


Figure B-4 REPRODUCIBILITY - PRECISION OF SAMPLES FROM RUN 1 (QA1)



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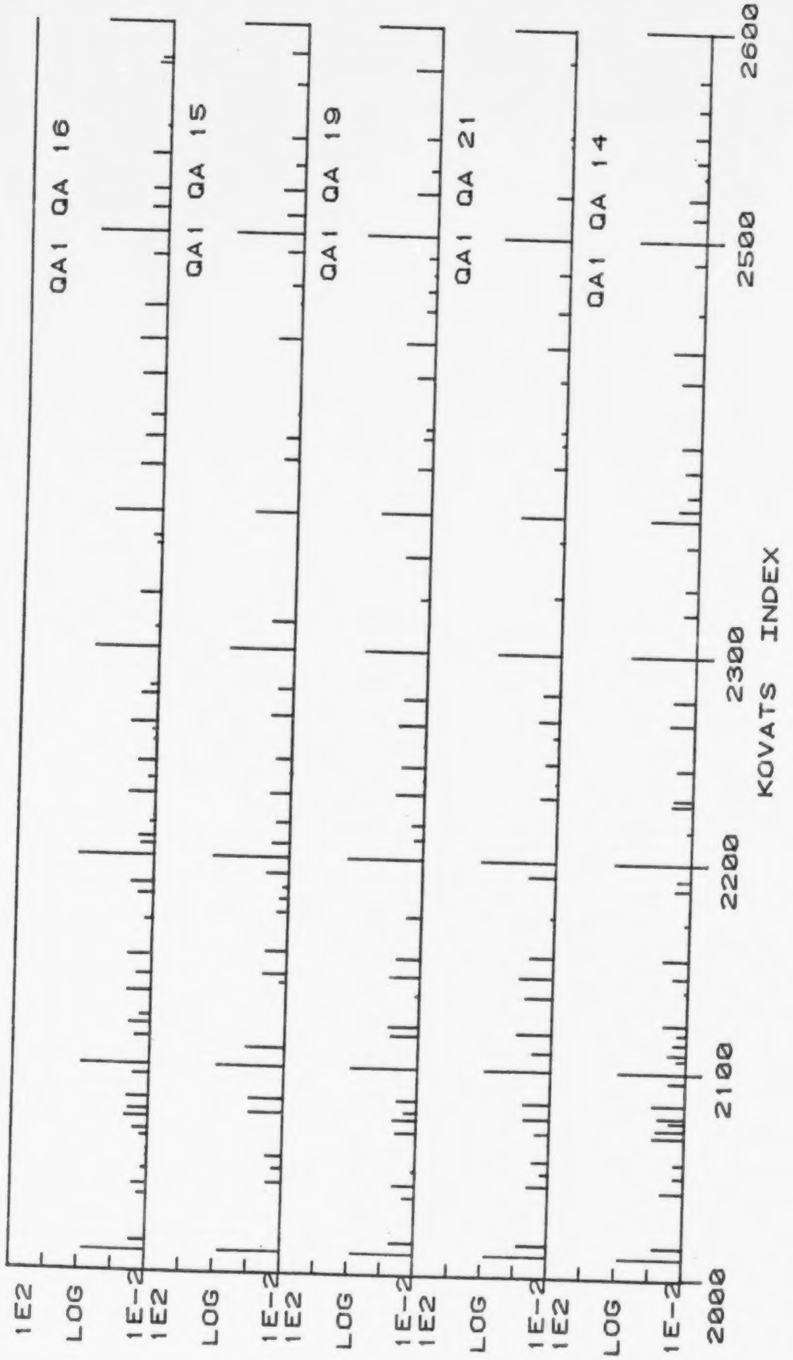

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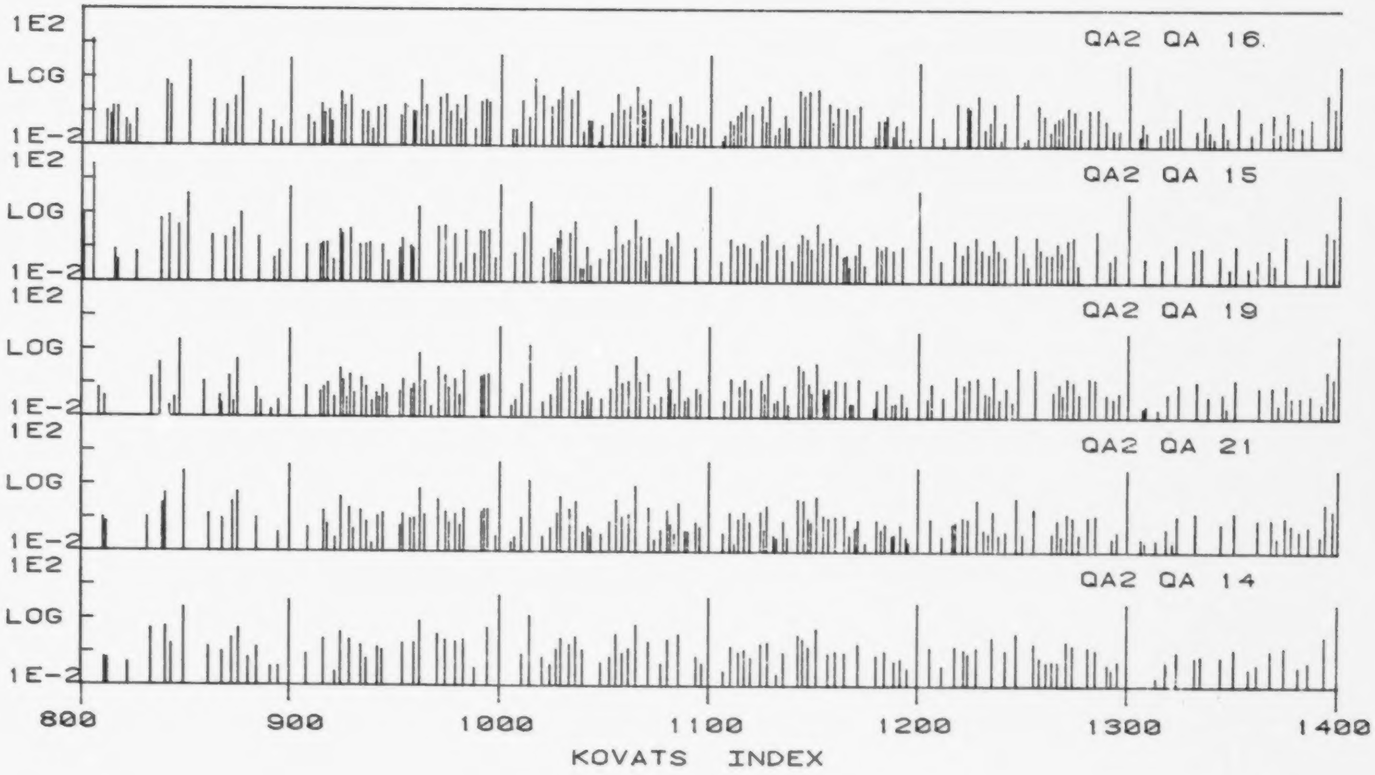
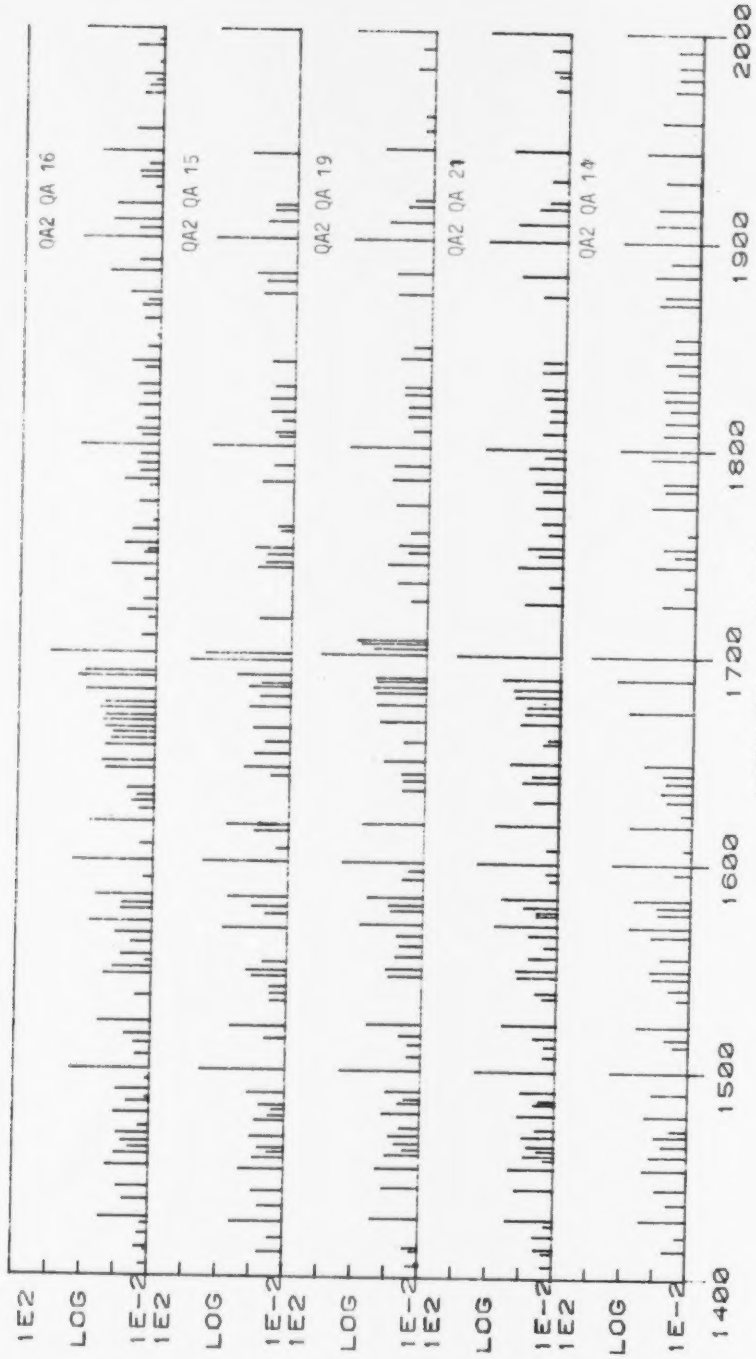


Figure B-5 REPRODUCIBILITY - PRECISION OF SAMPLES FROM RUN 2 (QA2)



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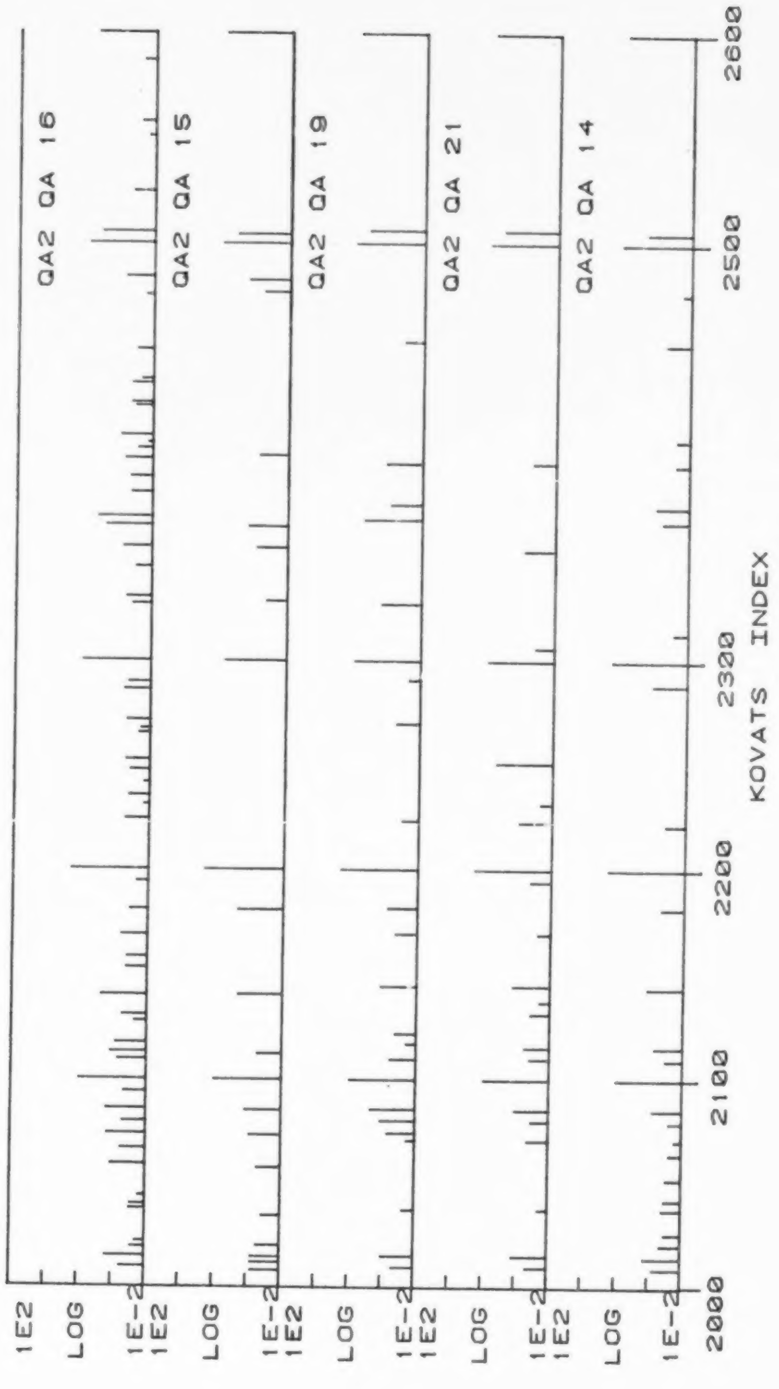

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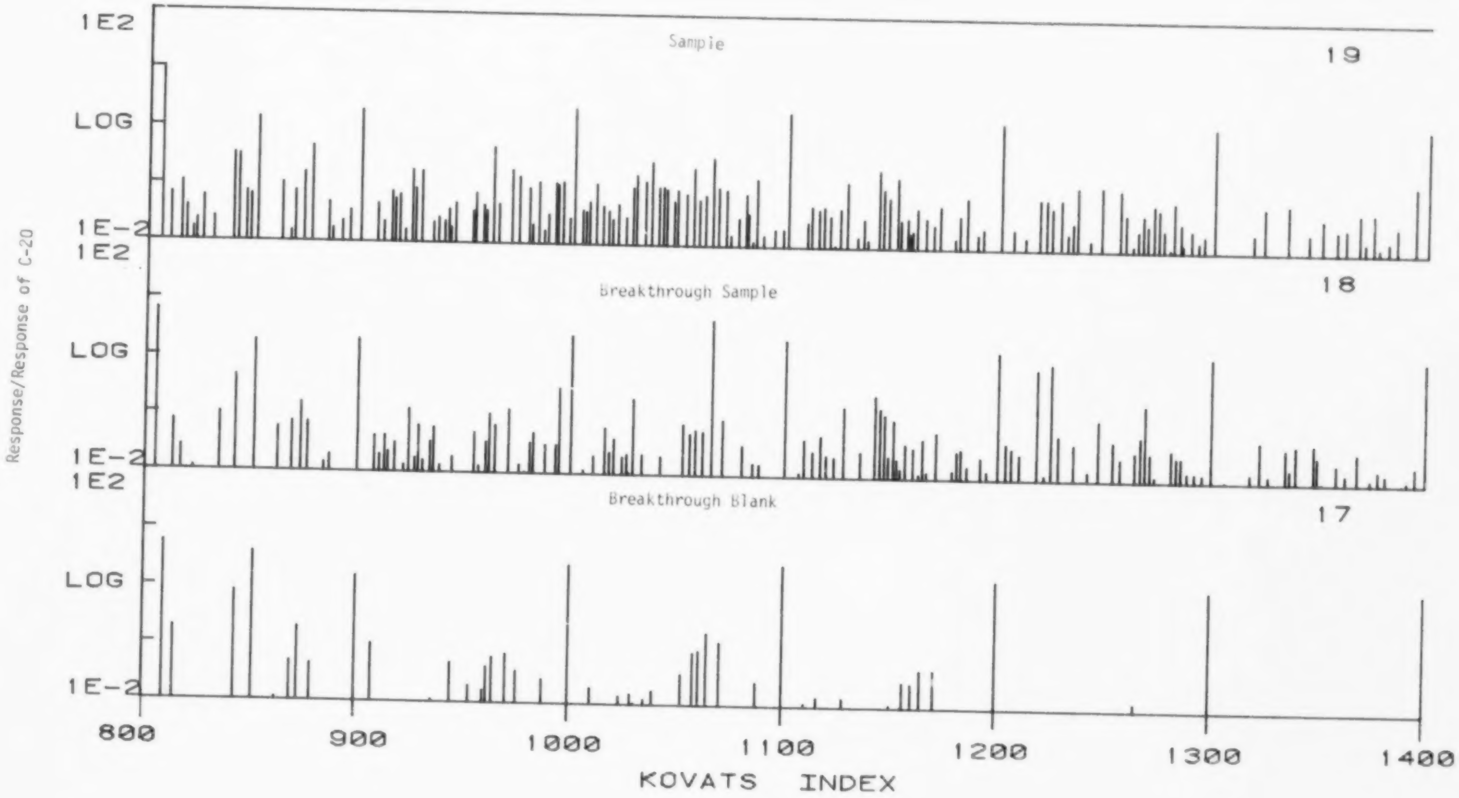

Figure B-6 BREAKTHROUGH OF ORGANICS ADSORBED ON XAD RESIN BED SAMPLERS AFTER 700 BED VOLUMES

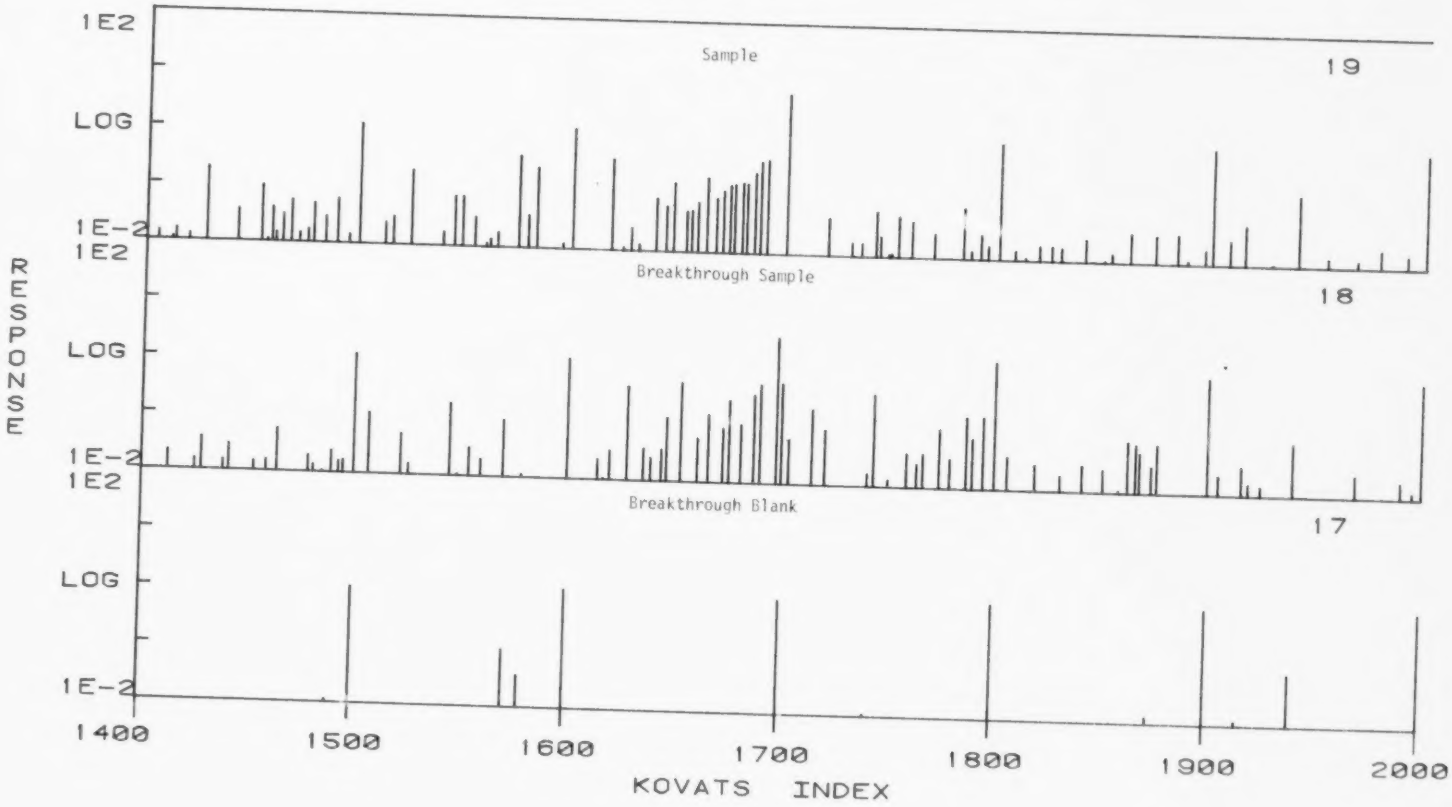

Figure B-6 (continued)

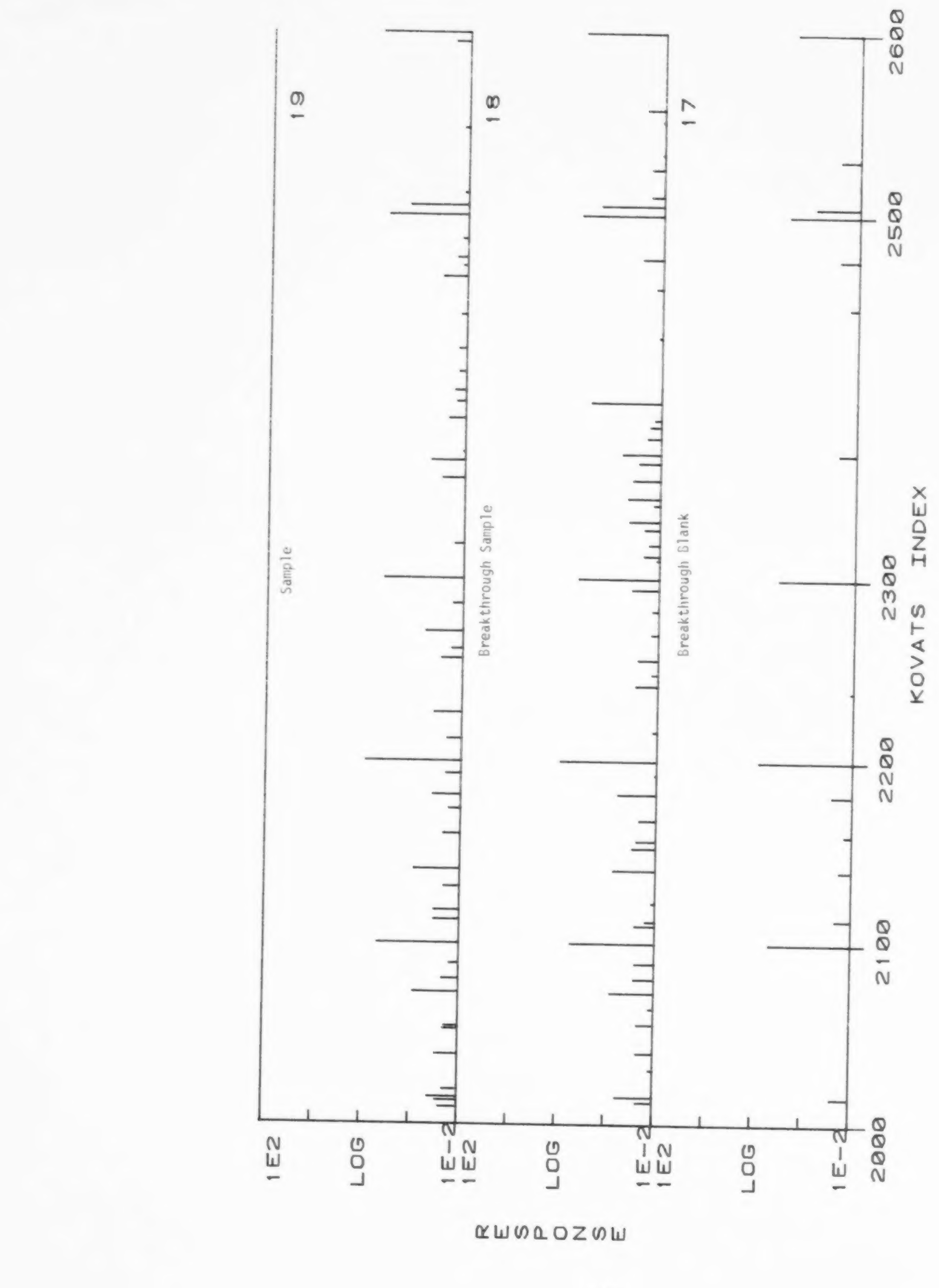

Figure B-6 (continued)

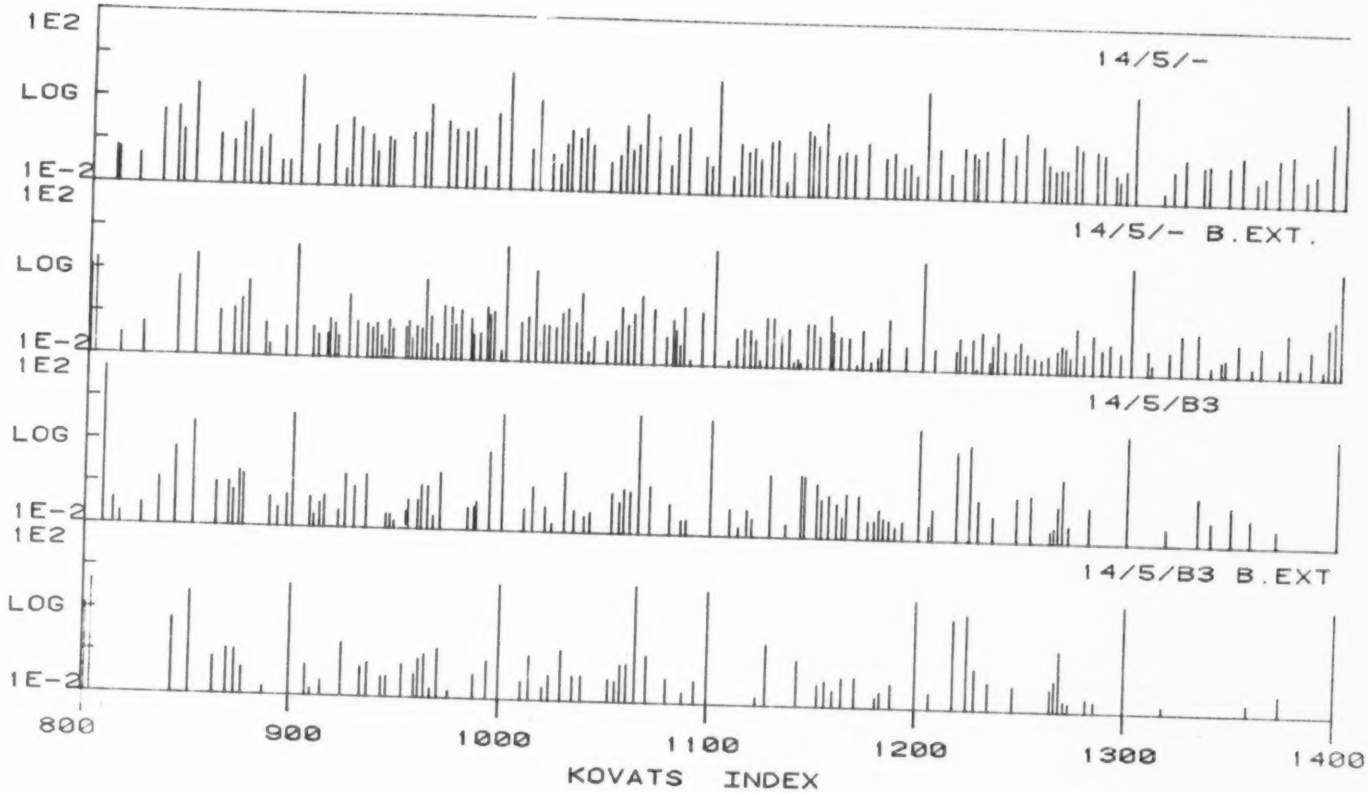

Figure B-7 EFFECT OF BASE EXTRACTION ON GC CAPILLARY CHROMATOGRAPHIC PROFILES

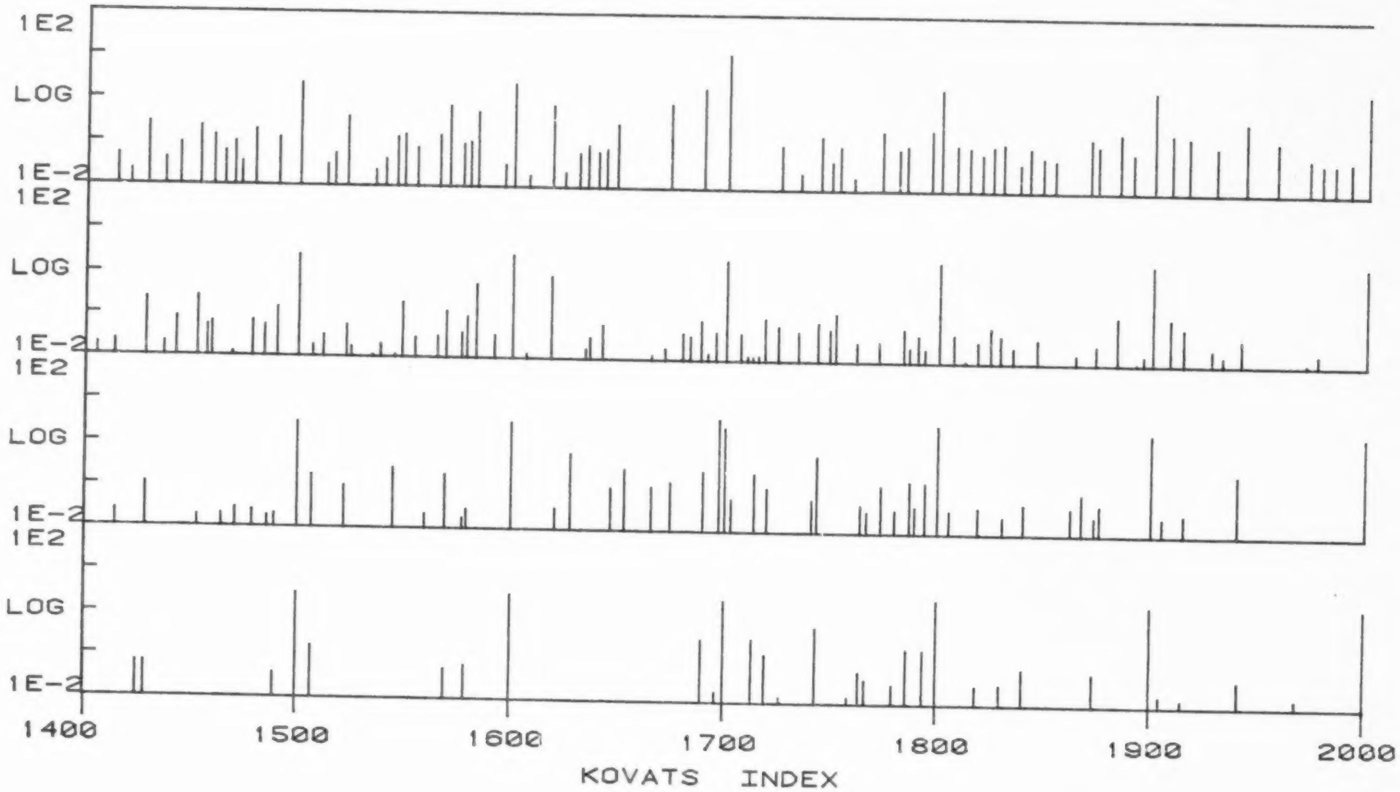

Figure B-7 (continued)

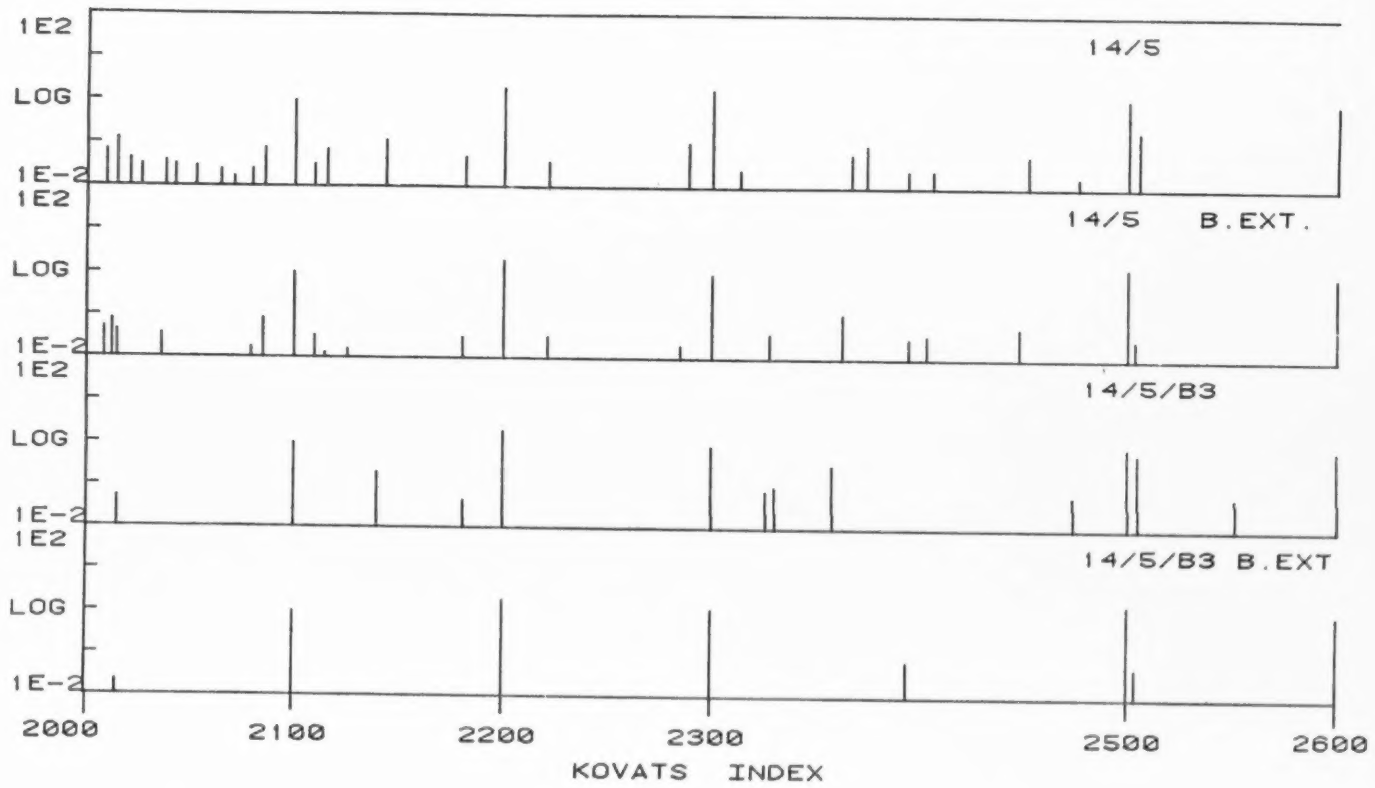

Figure B-7 (continued)

APPENDIX C

QUALITY ASSURANCE FOR MICROBIOLOGICAL STUDIES

ULTRA SONIC TECHNIQUE FOR ELUTION OF BACTERIA FROM GAC PARTICLES

The ultra sonic technique employed in this study was based on the ability of the ultra sonic unit to detach particles adhering to surfaces submerged in a solution in which ultra sonic vibrations are excited. This technique has been used successfully by Van der Kooij (119) of the Netherlands to elute bacteria from carbon particles. An in house study was conducted on this technique to determine the ultra sonic bath time necessary for maximum elution of bacteria from the carbon particles.

Nine granular activated carbon samples from the Torresdale preliminary GAC study were wet weighed and then placed into sterile capped test tubes containing 10 ml of sterile buffered water. These tubes were then placed into the ultra sonic cleaner (Branson Model B-3) which has a cleaning power of 40 watts. At the following intervals, 1, 2, 4, 8, 10, 15, 20, 25 or 30 minutes a sample was taken out of the bath. Each tube was shaken for one minute after which bacterial levels in the supernate were determined using the Soil Extract Agar Plate Count Technique. The results of this study can be found in Table C-1. As can be seen in this table, bacterial recovery rates increased with increasing ultra sonic bath time. Moreover, the same species of bacteria found in the GAC column effluents were also found on the carbon using the Ultra Sonic Technique.

TABLE C-1 ULTRA SONIC TECHNIQUE

COMPARISON OF ULTRA SONIC BATH TIME AND BACTERIAL RECOVERY

Ultra Sonic Bath Time	Ave. of 10 GAC Samples	S.D.
1 minute	$30 \times 10_6$	$25 \times 10_3$
2 minute	$41 \times 10_6$	$24 \times 10_3$
4 minute	$56 \times 10_6$	$33 \times 10_3$
8 minute	$62 \times 10_6$	$28 \times 10_3$
10 minute	$69 \times 10_6$	$39 \times 10_3$
15 minute	$82 \times 10_6$	$51 \times 10_3$
20 minute	$150 \times 10_6$	$53 \times 10_3$
25 minute	$179 \times 10_6$	$86 \times 10_3$
30 minute	$188 \times 10_6$	$69 \times 10_3$

TABLE C-2. COMPOSITION OF NITRIFYING BACTERIA MEDIA

$(NH_4)_2SO_4$ (Nitrosomonas only)	500 mg/l
KNO_2 (Nitrobacter only)	100 mg/l
$MgSO_4 \cdot 7H_2O$	50 mg/l
$CaCl_2 \cdot H_2O$	20 mg/l
$KHCO_3$	20 mg/l
K_2HPO_4	500 mg/l
NaCl	2000 mg/l
$NaMoO_4 \cdot 2H_2O$	2.419 ug/l

Trace Metals*

EDTA	2.5 mg/l
$ZnSO_4 \cdot 7H_2O$	10.95 mg/l
$FeSO_4 \cdot 7H_2O$	5.0 mg/l
$MnSO_4 \cdot H_2O$	1.54 mg/l
$CuSO_4 \cdot 5H_2O$	0.392 mg/l
$Co(NO_3)_2 \cdot 6H_2O$	0.243 mg/l
$Na_2B_4O_7 \cdot 10H_2O$	0.177 mg/l

*A few drops of H_2SO_4 are added to retard precipitation.

TABLE C-3. MEDIA COMPOSITION

R-2A Medium
Yeast Extract, 0.5 g
Proteose peptone No. 3, 0.5 g
Casamino acids, 0.5 g
Glucose, 0.5 g
Soluable starch, 0.5 g
K_2HPO_4, 0.3 g
$MgSO_4 \cdot 7H_2O$, 0.05 g
Sodium Pyruvate, 0.3 g
Agar, 15.0 g
Distilled water, 1l.
Adjust pH to 7.2 with crystalline K_2HPO_4 or KH_2PO_4 and sterilize at 121° C for 15 minutes.

Hugo Victorine Agar
Standard Methods Agar, 3 g
Agar, 12 g
Ferrous gluconate, 200mg
Distilled water, 1 L.
Adjust pH to 7.0 with crystalline K_2HPO_4 and sterilize at 121° C for 15 minutes.

Soil Extract Agar

Distilled water, 200 ml
Na_2CO_3, 0.2 g
African Violet soil, 77 g
Autoclave for 1 hour
Filter through paper before using in media

Nutrient Agar Solution, 750 ml
Soil Extract, 250 ml
Adjust pH to 7.0
Sterilize at 121° C for 15 minutes.

Standard Plate Count Agar
Plate Count Agar - Difco Laboratories-Cat. #0479-01-1

QUALITY ASSURRANCE PROGRAM

The quality assurance program used in this project followed the principals outlined in EPA's "Manual for the Interim Certification of Laboratories Involved In Analyzing Public Drinking Water Supplies, Criteria & Procedures, EPA 600/8-78-008, May 1978.

Laboratory Pure Water (Distilled & Deionized)

All water used in this project was subjected to the following analyses.

1. semi-annual analysis to determine the bactericidal properties of the distilled water. Procedures for this test can be found in "Standard Methods" 14th ed. p. 888. Corrective action was taken if tests exceeded the specified requirements and the water was retested.
2. semi-annual analysis for heavy metals in the water, especially Pb, Cd, Cr, Cu, Ni and Zn. Corrective action was taken if results exceeded specified requirements.
3. monthly analysis for conductanic, pH, chlorine residual and standard plate count. The standard plate count procedure can be found in "Standard Methods", 14th ed. p. 908-911. Plates were incubated at 35°±0.5°C for 48 hours.

Standard Requirements for Laboratory Pure Water

Conductivity	>0.2 megohms as resistivity or <5.0 micromhos at 25°C
Trace Metals:	
A single metal	Not greater than 0.05 mg/l
Total metals	Equal to or less than 1.0 mg/l

Test for Bactericidal Properties	0.8 - 3.0
Free Chlorine residual	0.0
Standard plate count	Less than 10,000/ml
pH	5.5 - 7.5

Quality Control of Laboratory Media, Equipment & Supplies

pH meter	Cleaned and calibrated with a ph 7.0 standard buffer. The buffer aliquot was used only once.
Balances	Calibrated annually by professionals
Hot air oven	Equipped with a thermometer calibrated in the range of 170°C. Records were maintained of the date, time and temperature of each sterilization cycle.
Autoclave	The date, time and temperature was recorded for each sterilization cycle. A heat sensitive tape was also used during each sterilization cycle to check sterilization efficiency. One bottle per sterilized bottle batch was checked for sterility by incubating 25 ml of sterile 2TB broth in it for 24 hrs at 35 ± 0.5°C and checking for growth.
Incubators	The air temperature of all incubators was recorded on a daily basis with in-place thermometers immersed in oil and placed on all shelves in use. These thermometers were checked annually against a certified thermometer.
Dish Washing	All glassware was washed with a non-toxic detergent (Sparkleen-Fisher Co.) The inhibitory residue test recommended by Standard Methods 14th ed. (p. 885) was conducted semi-annually and the results permanently recorded.
Media Preparation	The date, lot number, sterilization time and temperature, final pH and technicians name were recorded for each batch of media made up during this project. Positive and negative controls of E. coli were used to determine the recovery and performance of M-Endo Broth whenever a new lot number was used. Media was purchased in ¼ lb. bottles and any in use 6 months after opening were discarded.
Duplicate Analysis	Duplicate analyses on river samples were run once a month by each analyst in the lab. Results were recorded.

Methodology Quality Controls

Total Coliform Membrane Filtration Technique

1. A start and finish MF control test (rinse water, medium &

supplies) was conducted for each filtration series. When contamination occurred all data on affected samples were rejected.

2. Only plates with between 20-80 sheen colonies were counted. Plates with greater than 200 sheen and non-sheen colonies were also eliminated.
3. All sheen and borderline sheen colonies were verified in lauryl tryptose broth (LTB) and brilliant green lactose bile broth (BGLB). All positively verified colonies were also identified using the API 20 E system.

Soil Extract Agar Plate Count Technique

1. Control tests on the agar and dilution water were conducted for each new bottle of agar.
2. All samples were done in triplicate and results averaged.
3. Only plates with between 30 to 300 colonies were counted.
4. Melted medium was stored no longer than 3 hrs. before use.

Actinomycites Double Layer Agar Technique

1. Control tests on the agar and the dilution water were conducted for each series of samples.
2. All samples were done in triplicate and the results averaged.
3. Only plates with between 30 to 300 colonies were counted.

Fungii Plate Count Technique

1. Control tests on the agar and the dilution water were conducted for each series of samples.
2. All samples were done in triplicate and the results averaged.

APPENDIX D

OZONE MASS TRANSFER MODEL

A mathematical model for ozone mass transfer in a semibatch diffused gas contactor was developed in order to gain further insight into the ozonation process. The model is derived from the work of several authors (D-1, D-4). It was validated by comparison of the final output (a k_La) to the value obtained experimentally for the same parameter. For a series of three determinations, the experimental value was 1.72 ± 0.21 min^{-1} compared to a calculated model value of 1.32 min^{-1}. This sucessful validation step was taken to imply the validity of intermediate results. A flow chart, detailed description, sample input and output and a PDP BASIC program follow.

Experimentally, gas flow rate is measured by rotameter (Welsbach) which was calibrated by a wet test meter (precision scientific) and electronic timer (A.H. Thomas). Liquid volume was calculated from the height of the water column in the contactor (diffuser to meniscus) as measured by a laboratory meter stick. Total volume was calculated from the diffuser to liquid surface distance after gas flow was started and had reached a steady flow rate. Linear dimensions were measured by meter stick or micrometer. Diffuser pore size was obtained from the manufacturer (Kontes). Diffusivity was calculated by the method of Wilke and Chang (D-5). Physical constants of the aqueous matrix were obtained from standard references (D-5 and D-6). Ozone uptake and mass transfer measurements are described in the experimental section of the main body of this report.

Detailed Description:

1. The gas flow rate, column diameter, liquid/total volumes and physical properties all are input (in SI units)

   QG = gas flow
   DCOL = column diameter

2. Gas velocity (VG) is calculated

$$VG = 1.273 \left(\frac{QG}{DCOL^2}\right)$$

3. Gas holdup (GHU) is calculated from liquid volume (LVOL) and total volume (LGVOL) occupied by liquid and gas

$$GHU = \frac{LGVOL - LVOL}{LGVOL}$$

4. Superficial gas velocity (VS) is calculated and output

$$VS = VG/GHU$$

5. Gas density (GD), gas viscosity (MD) and orifice diameter of the diffuser (DO) are input and the mass flow rate calculated

$$MFR = (QG) \text{ X } (GD)$$

6. The orifice Reynold's number (REO) is calculated and output

$$REO = \frac{(1.273 \times MFR)}{(DO) \times (MD)}$$

7. Liquid (LD) and surface tension (TSURF) are input and bubble diameter (DP) calculated and output

$$DP = \left(\frac{0.612 \times (DO) \times (TSURF)}{LD}\right)^{1/3}$$

8. Specific interfacial area (A) is calculated and output

$$A = \frac{(GHU) \times 6}{DP}$$

9. The number of bubbles is calculated based on a spherical shape and output

$$N = \frac{A}{(3.14)(DP)}$$

10. Liquid diffusivity (DL) and viscosity (ML) are input and the Schmidt number for the liquid (SCL) calculated and output

$$SCL = \frac{ML}{(LD) \times (DL)}$$

11. The gas Reynold's number (REG) is calculated and output

$$REG = \frac{(DP) \times (VS) \times (LD)}{ML}$$

12. The liquid Sherwood number (SCL) is calculated and output

$$SHL = 2 + (0.0187)(REG^{0.779})(SCL^{0.546}) \text{ X}$$

where $X = \left(\frac{2.08 \times (DP)}{DL^{0.67}}\right)^{0.116}$

and the constants have been selected to represent swarms of bubbles rather than individuals.

13. Mass transfer coefficient (KL) is calculated and output

$$KL = \frac{(SHL) \times (DL)}{DP}$$

14. Overall mass transfer coefficient is calculated and output

$$KLA = (KL)(A)$$

after conversion from seconds to minutes.

Sample Input/Output

Input

QG = 0.5 SLPM

LGVOL = 658 mL

LVOL = 650 mL

GD = 0.665×10^{-5} Kg/m^3

DO = 50 microns

MD = 2.5×10^{-5} Kg/m-sec

LD = 1.0 g/cm^3

TSURF = 72.7 dyne/cm

DL = 1.74×10^{-9} m^2/sec

ML = 10^{-3} Kg/m-sec

DCOL = 2 cm

These values are converted to SI units and read into the program.

Output

VG = 2.65×10^{-2} m/sec

GHU = 1.22×10^{-2}

VS = 2.18 m/sec

REO = 7×10^{-2}

DP = 2.88×10^{-3}m (about 3 mm)

A = 25.4 m^2/m^3

$N = 2.8 \times 10^3$ bubbles

$SCL = 574$

$REG = 6.3 \times 10^3$

$SHL = 1440$

$KL = 8.7 \times 10^{-4}$ m/sec

$KLA = 2.2 \times 10^{-2}$/sec

$= 1.32$ / min

Computer program in PDP BASIC follows:

```
NEW

10   PRINT "THIS PROGRAM COMPUTES SYSTEM INTERFACIAL AREA AND INPUT GAS KLA
     FOR A SEMI-BATCH DIFFUSED AERATION DEVICE.  ALL PARAMETERS HAVE SI
     UNITS."

100  PRINT "DETERMINATION OF A"

110  PRINT "ENTER GAS FLOW RATE, COLUMN DIAMETER"

115  INPUT QG, DCOL

120  VG = 1.273 * (QG/DCOL 2)

125  PRINT "VG = " VG, "M/SEC"

130  PRINT "ENTER TOTAL VOLUME, LIQUID VOLUME"

135  INPUT 2 GVOL, LVOL

140  GHU = (LGVOL - LVOL)/LGVOL

145  PRINT "GAS HOLDUP" = GHU

150  VS = VG/GHU

155  Print "VS = " VS, "M/SEC"

160  PRINT "ENTER GAS DENSITY, VISCOSITY, ORIFICE DIAMETER"

165  INPUT GD, MD, DO

170  MFR = QG * GD

175  REO = (1.273 * MF)/(DO * MD)
```

```
176  PRINT "ORIFICE REYNOLDS # = " REO

180  PRINT "ENTER LIQUID DENSITY, SURFACE TENSION"

185  INPUT LD, T SURF

190  DP = (0.612 * DO * T SURF)/LD) ↑ 0.333

195  PRINT "BUBBLE DIAMETER = " DP, "M"

200  A = (6 * GHU)/DP

205  PRINT "AREA = " A, "PER METER"

210  N = A/(3.1416 * DP)

215  PRINT "N = " N "BUBBLES"

220  PRINT "DO YOU WANT TO CALCULATE INPUT GAS KLA (Y/N)?"

225  INPUT X$

230  IF X$ = "N" GO TO 375

235  PRINT "ENTER DIFFUSIVITY, LIQUID VISCOSITY"

240  INPUT DL, ML

250  SCL = ML/(LD * DL)

255  REG = (DP * VS * LD)/ML

256  PRINT "GAS REYNOLDS # = " REG

260  X = ((2.08 * DP)/(DL ↑ 0.67)) ↑ 0.116

265  SHL = 2 + (0.0187 * (REG ↑ 0.779) * (SCL ↑ 0.546) * X)

270  KL = (SHL * DL)/DP

275  PRINT "KL = " KL, "M/SEC"

280  KLA = KL*A

285  PRINT "KLA = " KLA "PER SEC"

286  PRINT "THE MASS TRANSFER COEFFICIENT IS   "  KLA * 60 "PER MINUTE"

375  STOP

380  END
```

REFERENCES

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D-5. Perry, R.H. & Chilton, C.H. Chemical Engineering Handbook, 5th Ed. McGraw Hill, NY. 1973.

D-6. Weast, R.C. ed. CRC Handbook of Chemistry & Physics, 51st ed. Cleveland, OH, 1971.

APPENDIX E

OZONATION OF MICROPOLLUTANTS

INTRODUCTION

This portion of the report is broken into three sections. The first section is Part A, Preliminary Methods, which describes the measurement of the mass transfer coefficient (k_La), Ozone Utilized and Saturation Ozone Concentration (C_{sat}) based on the Bunsen Coefficient. These techniques were used to examine the ozonation process.

Part B, Controlled Parameters Affecting Ozonation, is concerned with the first three steps in the micropollutant (Figure E-1) protocol. The paramters investigated were selection of the micropollutant, stripping vs. ozonation, and mass transfer vs. reaction rate controlled mechanisms. This section also determines the effect of ozone dose, pH and ionic strength on micropollutant ozonation.

The effect of water quality is dealt with in Part C. It completes the protocol by examining the effect of natural and processed waters on the ozonation of micropollutants.

Special attention is directed to the fact that most of the rate constants measured in this report are "process rate constants". These constants are measured for the ozonation of a micropollutant in a semi-batch bubble contactor. The rate constants measure the combined effect of ozone mass transfer and disappearance of a micropollutant.

Many of the ozonation experiments were performed in 0.2 M ionic strength phosphate buffers. Reactions in these buffers, especially at pH 8, served as a reference point. The effects of ozonation under various experimental conditions are determined with respect to the phosphate buffers.

Preliminary Analytical Methods

Calculation of k_La

In order to understand the interactions of ozone and micropoillutants in a semi-batch bubble diffuser contactor, it was necessary to assess the mass transfer characteristics of the contactor. The k_La, or the mass transfer coefficient, was measured in a contactor made from a Knotes chromoatographic column. In five trials, the value of k_La was determined to be $1.50 \pm 0.23\ \text{min}^{-1}$.

Calculation of Ozone Concentration in Solution

Although the ozone concentration in solution can be measured with the indigo technique, it was often necessary to predict the ozone saturation concentration without actual measurement.

The Bunsen Coefficient for ozone is 0.25 at 25°C (E-1). This temperature, 25°C, was the average aqueous temperature for waters ozonated in the laboratory. Generally, the temperatures ranged between 22° - 27°C. The ozone applied dose, measured by the KI method (E-2), was multiplied by 0.25 to obtain the saturation concentration of ozone in solution (ozone residual).

To test whether or not the Bunsen coefficient accurately predicted C_{sat}, ozone was bubbled through both pH 3 and pH 8 phosphate buffers, and the ozone residual measured after about 10 minutes of ozonation. The ozone applied dose had been previously measured. pH 3 and pH 8 were chosen as the ozone decomposition rates vary as a function of pH. For experimental surety it was necessary to confirm that the Bunsen coefficient would hold at both pH values.

The results are presented in Figure E-2. There is no significant difference between the ozone residual values at pH 3, pH 8, and the C_{sat} values predicted by the Bunsen Coefficient (F-test on slopes, $\alpha = 0.05$). It is apparent that pH does not affect the ozone residual and that the Bunsen Coefficient is a good predictor of saturation concentrations.

Controlled Parameters Affecting Ozonation

In this section the protocol is applied to the ozonation of toluene and diethylphthalate. The effectiveness of ozone in the removal of these micropollutants is evaluated. The effect of ozone dose, ionic strength and pH are also examined in relation to the removal of micropollutants during ozonation. A master rate equation is developed for predicting the rate constant for the ozonation of diethylphthalate.

Toluene

In accordance with the protocol, the first experiments performed with toluene consisted of comparing the rate of ozonation to the rate of oxygenation under the same pneumatic conditions. This was done to ascertain whether or not a stripping mechanism dominated in the removal of toluene.

Toluene possesses an absorbance maximum at 261 nm. This characteristic was utilized to follow concentration changes with a UV Spectrophotometer (2 cm cells). Beer's law is followed in the concentration range from 5 to 50 mg/L. See Table E-1. The shape and maximum of the toluene spectra did not change as a function of time of ozonation. This indicates that neither molecular O_3 or aromatic oxidation products were measured by the UV absorbance at 261 nm.

TABLE E-1. TOLUENE: BEER'S LAW

Concentration, mg/L	Absorbance @ 261 nm
50	0.080
40	0.073
40	0.073
30	0.058
20	0.039
10	0.019
5	0.011

$$\text{Concentration} = \frac{\text{Abs.} - 0.001}{0.00184} \qquad r^2 = 0.99$$

Duplicate analyses were performed with 600 ml of a 50 mg/L solution of toluene in pH 8 phosphate buffer. The results are presented graphically in Table E-2.

TABLE E-2. OZONATION AND OXYGENATION OF TOLUENE: 1ST ORDER REMOVAL RATE CONSTANTS

Ozonation, min^{-1}	Oxygenation, min^{-1}
0.299	0.365
0.268	0.528

A t-test indicated no significant difference at the 5% confidence interval. It is apparent that toluene is readily removed from solution by ozone and oxygen, with the rate of removal being approximately the same in both instances. Toluene is fairly volatile and can be expected to be removed by a stripping mechanism. McCarty and co-workers (E-3) state that compounds with Henry's Law Constants greater than 1×10^{-3} atm-m^3/mole are easily removed by stripping. The Henry's Law Constant for Toluene is 5.7×10^{-3} atm-m^3/mole. Later evidence indicates a chemical reaction is taking place between ozone and toluene. According to the protocol, however, if a micropollutant is successfully removed by stripping, it is not practical to consider oxidation by ozone therefore, toluene was not considered further.

Stripping of Diethylphthalate (DEP)

Since ozonation would not be feasible for the removal of toluene, diethylphthalate was chosen as the next micropollutant to be examined by the protocol. DEP is a slightly soluble organic with a very low vapor pressure. The Henry's Law Constant for this compound is 6.3×10^{-6} atm-m^3/mole (estimated from Reference E-3) and therefore it is not likely to be volatile.

As a first step in considering O_3 for the removal of DEP, a 15 mg/l, pH 8, 0.2M solution of DEP was subjected to a stripping analysis. DEP was followed by UV absorbance at 221 nm. The results are presented in Figure E-3. DEP is not well stripped by oxygen, although there is an initial sharp decrease in the DEP concentration, which quickly levels off. It is possible that this initial decrease in DEP is due to the action of O_3, but it is unknown why stripping would cause an immediate decrease and then no further effect. Another explanation could be adsorption of DEP onto the glass surface of the ozone contactor. DEP has previously been shown to exhibit significant adsorption onto glass (E-4). It is possible that DEP adsorbed rapidly onto the glass, saturated all the sites, and then exhibited no further decrease in concentration.

The initial decrease due to stripping and/or adsorption was about 5% of the initial concentration. This was not considered a significant amount. Therefore it was decided to proceed with the protocol and consider ozonation as a removal treatment for DEP.

Initial Rate of Ozonation of Diethylphthalate

The rate of disappearance of DEP was followed as a function of time of ozonation. The solution was 15 mg/l DEP in pH 8 0.2M phosphate buffer. The ozone applied dose was 2.30 mg/l O_3. DEP was followed by UV at 221 nm. In addition, the generalized products of ozonation were followed.

As can be seen in Figure E-4, ozonation significantly decreased the concentration of DEP in solution. The rate of decrease as followed by UV 221 nm was very rapid initially and then decreases. In order to ascertain whether the leveling off in the ozonation of DEP was real or the result of UV interference, it was decided to investigate possible UV interferences at 221 nm from probable products of ozonation (E-5, E-6). Glyoxylic Acid is a common product of ozonation of DEP by the Kramer Test. Oxalic acid is another frequently observed product of ozonation which has been demonstrated to be a resultant compound from the ozonation of phthalic acid (E-5, E-6). It is reasonable to assume that oxalic acid would also be a product of ozonation of diethylphthalate. Both oxalic acid and glyoxylic acid are fairly refractory to ozonation and would be expected to accumulate in solution during the ozonation process.

The molar absorptivities were measured in the laboratory for diethylphthalate, oxalic acid and sodium glyoxylate at 221 nm. These values were found to be 7720, 460, and 139 L/ cm-mole, respectively. At 221 nm, oxalic acid will absorb about 6% and glyoxylate about 2% of the light energy with respect to diethylphthalate at equimolar concentrations. Since concentrations of products are normally much less than DEP, it is unlikely that they will exert a great effect.

Non-specific parameters such as UV and also TOC, are extremely useful for qualitatively assessing the effect of ozonation, and generally speaking are convenient and easily applied analytical techniques. Caution must be exercised when using non-specific parameters since they measure overall changes and do not necessarily represent a pure compound.

The Kramer Test and the DNPH Test both measure low molecular weight carbonyl compounds, although the DNPH Test measures a greater number of compounds. Both of these tests indicate that a significant amount of the products are the typical aldehydes, ketones and carboxylic acids expected to be produced from the ozonation of organic compounds (E-7).

The Folin Test was employed to follow the hydroxylation of the aromatic ring. As seen in Figure 4-E, there is a slight initial increase in hydroxyaromatics and then no further increase as a function of ozonation. These results indicate that hydroxylation of the aromatic ring is probably a minor component of the ozonation of DEP at pH 8.

Total organic carbon, (TOC), was also monitored. Approximately 30% of the TOC was removed in 35 minutes.

For the analysis of ozonation of DEP at pH 8, the typical oxidized products of ozonation (i.e. carbonyl compounds) have been demonstrated. Hydroxylation of the aromatic ring appears to be a minor degradation pathway. TOC is substantially reduced.

Since UV proved ineffective for precisely measuring the disappearance of DEP, a GC method was developed using direct aqueous injection. The disappearance of DEP was again followed as a function of time of ozonation. The change in DEP concentration declined with time and did not level off as previously seen for the UV 221nm analysis. The first and second rate order constants were calculated for the disappearance of DEP. r^2 for first order was 0.988 and for the second order, r^2 equalled 0.977. It was therefore decided to use first order kinetics to calculate rate constants for the reaction of ozone with DEP.

Ozone Uptake

The first experiment performed to determine the process mechanism for ozonation of DEP was Ozone Uptake. Ozone in the gas phase was introduced into the contactor containing the micropollutant in solution. The ozone concentration in solution was measured as a function of time. This procedure is analogous to the method utilized to determine the k_La. The rate of ozone uptake is indicative of the process mechanism.

The theoretical mechanisms of ozone uptake are presented in Figure E-5. These mechanisms assume a stoichiometric excess of substrate. For the reaction rate controlled mechanism, ozone immediately appears in solution and quickly approaches the saturation concentration at a rate which approximates the k_La. In an ozone mass transfer limited reaction, no ozone appears in solution initially. With time, ozone accumulates in solution at a rate which is greatly less than that predicted by the k_La. The third case, a quasi mass transfer reaction, is intermediate between the other two reaction mechanisms. Ozone Upatake was measured at both pH 3 and pH 8 for a 6.75×10^{-2} mmole/L solution of DEP in 0.2 M phosphate buffer. The results are presented in Figures E-6 & E-7.

At pH 3 ozone was immediately measured in solution and rapidly reached a steady state concentration. For pH 8 there was an initial lag in ozone uptake so that the concentration of ozone in solution remained very low for approximately the first seven minutes. After this lag the ozone concentration increased at a rate less rapid than at pH 3, and finally reached about the same steady state concentration as pH 3.

Applying a first order model, process rate constants for uptake of ozone into a solution of DEP were calculated for pH 3 and pH 8. These rate constants are calculated by the same equation as used to calculate the k_La. The data for these rate constants are presented in Table E-3.

TABLE E-3. RATE OF OZONE UPTAKE (k_V) AT pH 3 and pH 8 FOR DEP

k_V, min^{-1} (pH3)	k_V, min^{-1} (pH 8)
0.77	0.16
1.95	0.15
$k_V = 1.36 \pm 0.84$	$k_V = 0.16 \pm 0.01$

The difference between ozone uptake at the acidic and the basic pH values is significant. If the rate constants for ozone uptake in the presence of DEP are compared to the k_La measured for this contactor, i.e., $1.50 + 0.23$ min^{-1}, it is found that there is no significant difference at pH 3, but there is a statistically significant difference at pH 8 (t-test, $\alpha = 0.05$ for both pH values).

When comparing the ozonation of DEP at pH 3 to that at pH 8, it appears that two different ozonation mechanisms are operating. For pH 3, the immediate and rapid disappearance of ozone in solution coupled with the slow disappearance of DEP suggest a reaction rate controlled mechanism. For pH 8, the slow ozone uptake curve in conjunction with the fast removal of DEP indicate a mass transfer controlled mechanism.

At pH 3, ozone is stable as the O_3 molecule and reacts through a direct ozonation mechanism which is a slow ionic attack (E-8). This is most likely the chemical mechanism of reaction at pH 3. Diethylphthalate is deactivated with respect to electrophilic attack due to the two ester groups on the benzene ring, and therefore not readily susceptible to direct oxidation by ozone. It appears that DEP is somewhat refractory to ozonation at low pH, and the ozonation to remove DEP would be inefficient.

Rates of Reaction of Diethylphthalate as a Function of Ozone Dose

In order to further examine the effect of mass transfer on the ozonation of DEP at pH 8, a series of experiments were performed at various ozone doses. Varying the ozone dose affects the (C_{Sat} −C) term in the mass transfer equation. The rate of disappearance of DEP was monitored by GC analysis and the first order process rate constants calculated as a function of time. Table E-4 presents the data.

TABLE E-4. EFFECT OF OZONE DOSE ON THE OZONATION OF DEP AT pH 8

Applied Ozone Dose mg/L O_3	C_{sat} (calculated) moles/L O_3	k_{DEP} min^{-1}
2.01	0.0105	0.214
2.60	0.0135	0.277
2.77	0.0145	0.256
5.28	0.0275	0.408
6.81	0.0355	0.659

Since the DEP concentration and pH were held constant, an apparent rate for the reaction of DEP as a function of ozone dose can be calculated. The equation used was:

$$\log k_{DEP} = \log k' + n \log [O_3]$$

where: k_{DEP} = the measured first order rate constant, in min^{-1}
$[O_3]$ = calculated from C_{Sat}, mmoles/L
log k'= the y-intercept and is the log of the apparent rate constant for a constant DEP concentration and pH
n = the slope of the curve log k_{DEP} vs. log $[O_3]$ this is equal to the reaction order with respect to $[O_3]$

With the appropriate numerical values this equation is:

$$k_{DEP} \text{ (estimated)} = 9.95 \times [O_3]^{0.848} \quad ; \quad r^2 = 0.971$$

An attempt was made to examine the initial rate of input of O_3 and the initial rate of removal of DEP. The equation applied is:

$$dO_3/dt = k_La\,(C_{Sat} - C) - k_{DEP}\,[DEP] \times (mM\ O_3/mM\ DEP) - k_d''\,[O_3]$$

where k_d'' = the first order rate constant for the decomposition of O_3 (E-9)
mMO_3/mM DEP = stoichiometric ratio which relates the moles of O_3 consumed to the moles of DEP removed.

During approximately the first minute of reaction there is no ozone in solution at pH 8. (See Figure E-7). This means that initially dO_3/dt = zero. Furthermore, since no ozone is in solution, $C_t = 0$ and therefore the ozone input rate can be approximated by k_La (C_{Sat}).

k_d'' [O_3], as mentioned before is the relationship for the decomposition of ozone. At pH 8 $k_d'' = 8.83 \times 10^{-2}$ min^{-1} (E-9). In each case the ozone decomposition was found to be at least two orders of magnitude less than the input of ozone of the disappearance of DEP. The effect of ozone decomposition is therefore negligible in this comparison.

The final term to be discussed is k_{DEP} (DEP) x (mM O_3/mM DEP). k_{DEP} was measured and the initial concentration of DEP was 6.75×10^{-2} mM. The ratio mM O_3/ mM DEP represents the stoichiometric equivalence ratio for the reaction of DEP and O_3, and is assumed to be one.

Now it has been demonstrated that $dO_3/dt = 0$, $C_t = 0$, k_d'' [O_3] can be assumed negligible, and mM O_3/ mM DEP is 1. The initial equation then reduces to k_La (C_{Sat}) = k_{DEP} (DEP). In other words, the initial ozone mass transfer can be compared to the initial rate of DEP removal. The calculated values are listed in Table E-5.

TABLE E-5. COMPARISON OF INITIAL MASS TRANSFER AND DEP REMOVAL

O_3 Applied Dose; mg/L O_3	Ozone Mass Transfer; mmoles O_3/L-min	DEP Removal mmoles DEP/L-min	% Difference 1 - O^3/DEP
2.01	0.0158	0.0144	9
2.60	0.0202	0.0187	7
2.77	0.0218	0.0173	20
5.28	0.0412	0.0275	33
6.81	0.0532	0.0439	17

The rate of initial ozone mass transfer is consistently greater than the rate of DEP removal when a 1:1 relationship is assumed for O_3; DEP. Both reaction rates are of the same order of magnitude and only differ by about 17%.

Non Mass Transfer Reactions

As a final experiment to determine the mechanism controlling the reaction of DEP at pH 3 and pH 8, the rate of disappearance of DEP was followed in a non-mass transfer situation. Under these conditions ozone in solution at pH 3 or pH 8 was introduced into a stir-tank reactor containing DEP in solution at either pH 3 or pH 8. Samples were taken as a function of time and analyzed by GC. Sodium sulfite was added to the sampling vials to reduce residual ozone at the time of sampling. Ozone residual was monitored also. The data are presented in Tables E-6 and E-7.

TABLE E-6. NON MASS TRANSFER REACTIONS

pH 3

Time, min	Ozone Residual, mmoles/L	DEP, mg/L
0*	0.044	6.0 ± 0.35**
0.08		6.1 ± 0.45
0.25	0.038	
0.5		6.28 ± 0.25
1.5	0.033	
3		5.69 ± 0.16
3.5	0.031	
7.5		5.66 ± 0.08
8	0.022	
10		5.19 ± 0.32
10.5	0.014	
13.5	0.012	
14		4.75 ± 0.17
16	0.012	

* Time zero represents a sample before the addition of ozone and acts as a standard

** The mean ± standard deviations are given for the GC analysis data and represent repeated injections of the same sample into the GC. Generally each sample was analyzed four times.

TABLE E-7. NON MASS TRANSFER REACTIONS

pH 8

TRIAL I[***]		TRIAL II	
Time, Min	DEP, mg/L	Time, Min	DEP, mg/L
0[*]	6.0 ± 0.12[*]	0[*]	6.0 ± 0.26[**]
0.08	3.18 ± 0.05	0.008	4.0 ± 0.02
1	3.14 ± 0.08	2	3.32 ± 0.28
4	3.16 ± 0.007	3	3.45 ± 0.31
		5	3.15 ± 0.08
no ozone residual was measured in solution		no ozone residual was measured in solution	

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[*] Time zero represents a sample before the addition of ozone and acts as a control

[**] The mean ± standard deviations are given for the GC analysis data and represent repeated injections of the same sample into the GC. Generally each sample was analyzed four times.

[***] Sodium sulfite was not added to these samples

Statistical analysis was performed with a one way Analysis of Variance (ANOVA) at pH 3. There was a significant difference between all sampling times, 0 to 14 minutes ($\alpha = 0.05$). The first order rate constant for the disappearance of DEP at pH 3 was calculated to be 0.017 min^{-1} ($r^2 = 0.985$).

At pH 8 an ANOVA for Trial I was performed to evaluate only the ozonated samples, times 0.08 to 4 minutes. At the 95% confidence interval no difference was found. These ozonated samples clearly contain a lower concentration of DEP than the control at time 0 min, indicating that the reaction of ozone and DEP in a non mass transfer situation was instantaneous. A first order rate constant was not calculated due to insufficient data points at critical times.

For Trial II at pH 8 an ANOVA demonstrated that there is a significant difference between the ozonated samples at times 0.08 to 5 minutes ($\alpha = 0.05$), although these samples again contain a lower concentration of DEP than the control. This could be taken to indicate that the initial reaction of ozone and DEP is extremely fast, but does not go instantly to completion.

Summary

The three previous experiments, namely Ozone Uptake, Rate of Reaction of Diethylphthalate as a Function of Ozone Dose at pH 8, and Non Mass Transfer Reactions were all performed with the intent of understanding the mechanism of reaction between ozone and diethylphthalate. The conclusions are that at pH 3 the reaction is a reaction rate controlled reaction, whereas at pH 8 it is mass transfer controlled. Supporting evidence comes from:

pH 3		pH 8
1) Ozone Uptake is instantaneous in a bubble contactor with mass transfer	* * *	1) Ozone Uptake displays an initial lag period and then is slowly taken up in a mass transfer situation
2) When both ozone in solution and DEP in solution are combined there is a slow reaction	* * * *	2) Under non mass transfer conditions the reaction between ozone and DEP is almost instantaneous
	* * * *	3) The reaction rate of O_3 and DEP increases proportional to increased mass transfer

The pH values intermediate between pH 3 and pH 8 are expected to represent a transition from a reaction rate to a mass transfer controlled mechanism. It is not possible to predict the point at which this transition occurs based on the experimental results presented. Acidic pH values probably contain more of the reaction rate control characteristics whereas basic pH values are mass transfer controlled.

Ozone Utilized

Ozone Utilized was determined for pH 3 and pH 8 phosphate buffers with and without the presence of DEP. The results are presented in Table E-8. Each value represents the average of four measurements.

TABLE E-8. OZONE UTILIZED

Sample	Ozone Utilized mg O_3/ L solution
pH 3 Buffer	-0.07 ± 0.789
pH 3, w/ DEP	1.25 ± 1.30
pH 8, Buffer	1.18 ± 0.21
pH 8, w/ DEP	5.80 ± 1.51

The ozone utilized at pH 3 with and without DEP is not significantly different (student t-test, $\alpha = 0.05$), while at pH 8 there is a statistical difference. The ozone utilized at pH 8 in the presence of DEP is significantly different from that utilized at pH 3 w/DEP (t-test, $\alpha = 0.05$).

The concentration of DEP in solution was measured to be zero after fourteen minutes of ozonation at pH 8 during the measurement of ozone utilized. It is possible to estimate a stoichiometric coefficient relating the amount of ozone consumed to the amount of DEP removed. When utilized by buffer alone, this coefficient is 1.42 mmoles O_3/ mmoles DEP. 1.42 represents a process stiochiometric coefficient which includes the reaction of ozone and DEP as well as ozone and the organic degradation products of DEP. It is likely that the reaction between ozone and DEP alone would have a coefficient of less than 1.42.

Effects of pH on the Reaction Rate of DEP

To determine the effect of pH on the process rate, 0.2 M phosphate buffers containing DEP were ozonated at an ozone applied dose of 2.68 ± 0.05 mg/l. Duplicate analyses were performed. The results are presented in Table E-9.

TABLE E-9. EFFECT OF pH ON OZONATION RATE

pH	1st Order Rate Constant (min^{-1})	
3.00	0.005	($r^2 = 0.362$)
6.07	0.137 ± 0.005	($r^2 = 0.99$)
6.89	0.177 ± 0.018	($r^2 = 0.997$)
8.14	0.256 ± 0.029	($r^2 = 0.993$)
9.06	0.259 ± 0.025	($r^2 = 0.976$)

There is no significant difference (t-test, $\alpha = 0.05$) between the ozonation rate constant at pH 8 and pH 9. Other than the pH 9 result, the rate of ozonation of DEP increases as a function of pH. This is to be expected based on previous results which demonstrated a large difference between the ozonation of DEP at pH 3 and pH 8.

Master Rate Equation

A master rate equation was developed to calculate the first order rate constant for the ozonation of diethylphthalate as a function of pH and ozone applied dose. The master rate equation utilizes the rate orders previously calculated for pH and ozone applied dose. This equation is based on the well-known facts that the reaction of most aromatic compounds with ozone is first order with respect to compound and ozone and additionally, depends on ozone decomposition rate (E-16)., a function of hydroxide ion concentration. The equation was experimentally derived by pseudo-first order isolation of variables. For example, if the concentration of diethylphthalate is held constant and under conditions of constant applied ozone dose, pH, as expressed by the hydroxide ion concentration, may be varied. The data from this experiment allows for determination of the order of the reaction through evaluation of the exponential parameter and the rate constant. It was decided that hte most useful from of this equation is one in which the function dependence of the rate on the diethylphthalate concentration is eliminated. The reaction is considered to be first order with respect to DEP concentration. Basically this overall equation possesses the form of:

$$d[DEP]/dt = k_{app}\ [DEP]^1\ [O_3]^{0.848}\ [OH^-]^{0.142} \quad \text{in mM/L-min}$$

where all concentrations are measured in millimoles/L

k_{app} = a numerical coefficient and represents the apparent rate constant

In order to solve for k_{app}, the first order rate constants measured for the ozonation of DEP in various pH buffers and at various ozone doses were plotted against the calculated factor

$$(\ [O_3]^{0.848} \times [OH^-]^{0.142}\ )$$

This factor was calculated at the actual concentration values applied in each ozonation experiment. The slope of this line is the value of k_{app}. The units of k_{app} are whatever fractional inverse of mmoles/L necessary to allow k_{DEP} to be calculated in min^{-1}. The final equation is:

$$k_{app} = 27.9$$

$$k_{DEP} = 27.9 \times [O_3]^{0.848}\ [OH^-]^{0.142} \quad , r^2 = 0.97$$

where all concentrations are measured in mmoles/L and
k_{DEP} is calculated in min^{-1}

The purpose of this equation is to allow for the calculation of predicted process rate constants. The Master Rate Equation accounts for variation due to pH and ozone dose only. The value of this equation is that rate constants measure for the ozonation of DEP in various aqueous media can be compared to rate constants predicted at that particular pH and ozone dose. If the measured rate constant differs from the predicted, that means that some factor other than pH or O_3 dose is responsible for the effect.

It should be noted again that the rate constants measured and predicted are process rate constants for the interaction of ozone and diethylphthalate. These rate constants measure the rate of disappearance of DEP as a function of ozone mass transfer as well as reaction with ozone itself.

A problem with the master rate equation is that it lacks provision to perform statistical analysis. If the error in the predicted rate constant can be calculated, then it can be statistically compared to the experimentally measured values. To evaluate the error in the master master rate equation,

$$k_{DEP} = k_{app} \times [O_3]^{0.848} \; [OH^-]^{0.142}$$

the following error analysis will be applied. Δk_{DEP} is the error in the predicted rate,

$$\Delta k_{DEP} = \left| \frac{\partial k_{DEP}}{\partial k_{app}} \right| \Delta\, k_{app} + \left| \frac{\partial k_{DEP}}{\partial O_3} \right| \Delta\, O_3 + \left| \frac{\partial k_{DEP}}{\partial OH^-} \right| \Delta\, OH^-$$

If the indicated differentiations are performed, the solutions are:

$$\frac{\partial k_{DEP}}{\partial k_{app}} = [OH^-]^{0.142}[O_3]^{0.848}$$

$$\frac{\partial k_{DEP}}{\partial O_3} = [OH^-]^{0.142}(0.848)[O_3]^{-0.152}(k_{app})$$

$$\frac{\partial k_{DEP}}{\partial OH^-} = 0.142[OH^-]^{-0.858}[O_3]^{0.849}(k_{app})$$

a 5% error is assumed for the measurement of k_{app} and $[O_3]$; a 2% error is assumed in the measurement of $[OH^-]$. The variables and typical values are listed below.

VARIABLE	VALUE	ERROR
k_{app}	27.9 min^{-1}	1.4 min^{-1}
O_3	0.0139 mM	7 x 10^{-4} mM
OH^-	10^{-3} mM	2 x 10^{-5} mM

This method of evaluating the error in the predicted rate constant will be utilized throughout the text.

Effects of Ionic Strength

An experiment was performed to assess the effect of ionic strength on the rate of ozonation of DEP. The medium for the ozonation was pH 8 phosphate buffer at 0.2, 0.02, and 0.002 molar ionic strengths. Samples were taken as a function of time for up to ten minutes. The results are presented in Table B2-10.

Table E-10. EFFECT OF IONIC STRENGTH ON REACTION RATE

Ionic Strength(M)	Rate(min^{-1})	Initial pH	Final pH	Δ pH
0.2	0.276	8.17	8.14	-0.03
	0.235		8.14	-0.03
0.02	0.257	7.94	7.81	-0.13
	0.255		7.85	-0.09
0.002	0.199	7.81	7.30	-0.51
	0.177		7.52	-0.29

As can be seen, the change in ionic strength from 0.2M to 0.02M did not affect the overall rate of ozonation of DEP, whereas the drop to 0.002M significantly reduced the rate of ozonation. The change in pH before and after ozonations also varied as a function of ionic strength. It was intended that all the buffer samples be at pH 8 initially. Unfortunately, the 0.02M and 0.002M solutions were serial dilutions of the 0.2M solution and the pH was not readjusted after the addition of distilled water. In spite of this, the change in pH still varied with ionic strength which, in this instance, was proportional to the buffer capacity of the solution. Thus it appears that the lower rate with respect to the 0.002 M solution is due to a lower pH rather than a true ionic strength effect.

There are, however, several other hypotheses which may serve to explain this phenomenon. The first of these is based on ozone mass transfer. There is an important correlation between mass transfer rate and bubble size (E-13). The addition of a neutral salt to water will alter the viscosty, surface tension, density and gas diffusivity (See appendix D) with the net effect of reducing bubble size, increasing specific interfacial area and increasing mass transfer. Thus, the slower rate with the most dilute solutions may also be due to larger bubbles and consequent diminished mass transfer in addition to the pH effect.

A second alternate hypothesis might argue that the effects are due to phosphate itself rather than hydroxide ion. Although polyoxy anion catalysis of ozone decomposition may be a possibility, there is a preponderance of evidence with indicates that this is not a significant effect when compared with the large effect exerted by hydroxide ion. Phosphate salts have a long history of use as buffers in rigorous ozone kinetic studies (E-14); it has been found that, when compared with other ions such as carbonate and tetraborate that the rate of ozone decomposition is slowest with phosphate (E-15); results from this laboratory show that, at pH 2, the rate of ozone decomposition is the same in phosphate as the rate in a non-participating chlorate system.

It light of the evidence compiled both in the laboratory and in the literature, it appears possible to conclude that the diminished pH is the primary effect iwth ozone mass transfer possibly being a secondary one.

Statistically, an ANOVA demonstrated that there was a significant difference between ionic strength and reaction rate ($\alpha = 0.05$). The difference between 0.2M and 0.02M was shown not to be significant by the t-test ($\alpha = 0.05$).

Effect of Natural and Processed Waters

The final step in the protocol is to evaluate the effect of organic and inorganic compounds present in the water supply on the ozonation process. Together these constitute the total matrix or water quality effect. This section will examine the effect of river water, inorganic constituents of river water, and processed or partially processed drinking water on the ozonation of DEP. The purpose here is to determine which factors have the greatest effect and whether or not these factors can be controlled.

Effect of River Water

Diethylphthalate was ozonated in the presence of Delaware River water, Delaware River water filtered through glass fiber filter to remove particulates, and Simulated Delaware River (SDR) water made up from inorganics only.

The purpose of ozonating DEP in river water was to assess the total matrix effects. Following this, filtered river water was examined to determine the effect of suspended solids. Lastly, SDR was evaluated to assess the effect of the inorganic compounds alone. The analysis consisted of monitoring the rate of disappearance of DEP and the change in pH upon ozonation. Predicted rate constants for ozonation were calculated based on the master rate equation employing the average pH. Standard deviations for these predicted rates were calculated.

Comparisons of the predicted rate constants vs. the experimentally measured rate constants were done based on t-tests, $\alpha = 0.05$. The data are presented in Table E-11.

TABLE E-11. OZONATION OF RIVER WATER

Sample	Initial pH	-	Final pH	Δ pH	Measured k_{DEP} (min^{-1})	Predicted k_{DEP} (min^{-1})
River	7.58	-	7.62	+0.04	0.170	0.242 ± 0.017
	7.64	-	7.71	+0.07	0.186	0.251 ± 0.018
Filtered	7.52	-	7.60	+0.08	0.161	0.241 ± 0.017
River	7.73	-	7.63	-0.11	0.147	0.250 ± 0.018
SDR	7.63	-	7.38	-0.25	0.186	0.237 ± 0.017
	7.63	-	7.31	-0.32	0.173	0.235 ± 0.016

(Ozone Applied Dose = 2.67 ± 0.04 mg/L, or 0.0139mM)

There is a significant difference between the measured and predicted k_{DEP} values for all three experiments. This indicates that the measured rates of ozonation were significantly less than would be expected under ideal ozonation conditions in phosphate buffers. This reduction in rate is related to the river or simulated river matrix.

ANOVA of the three sets of experimentally measured rate constants indicates that there is no significant difference between these values ($\alpha = 0.05$). The pH change is the greatest for SDR, and somewhat less for the river waters.

Effects of Inorganic Compounds

From the previous section it is evident that inorganic compounds can exert an effect on the ozonation of DEP. To investigate a few possible causes of this rate reduction, DEP was ozonated in the presence of bicarbonate, iron, and kaolinite.

A 0.02 M $NaHCO_3$ solution was examined as the carbonate system is the principle buffering agent for the Delaware River. It is expected that bicarbonate (the predominant species at the pH of the river, i.e., pH 6.8 to pH 7.8) would act to scavenge hydroxyl radicals and decrease the rate of ozonation (E-10). Ammonia, another inorganic predicted to interfere with ozonation, was not investigated as it is the NH_3 species which interferes and this species is insignificant at the pH of the Delaware River (E-10).

Kaolinite, the principle clay in the Delaware, was investigated to assess the effect of particulates. 0.5 grams were added to a 0.02 ionic strength phosphate buffer at pH 8.

Iron was also investigated as it was suggested that iron salts have a catalytic effect on the ozonation process (E-11). Non-soluble iron is generally present at 1 mg/L in the Delaware River. To mimic this, approximately 1 mg/L of electrolytic iron flakes were suspended in 0.02 M ionic strength phosphate buffer at pH 8.

All of these experiments were performed with an average ozone dose of 2.67 ± 0.04 mg/L O_3, and compared to the ozonation of DEP in 0.02 M phosphate buffer. The results are presented in Table E-12.

TABLE E-12. EFFECT OF INORGANICS ON THE OZONATION OF DIETHYLPHTALATE

SAMPLE	INITIAL pH	-	FINAL pH	Δ pH	MEASURED k_{DEP}**	PREDICTED k_{DEP}**
Phosphate	7.94	-	7.81	-0.13	0.257	0.267
Buffer*	7.94	-	7.85	-0.11	0.255	0.269
Carbonate	8.25	-	8.83	+0.58	0.036	0.277
Buffer*	8.25	-	8.75	+0.50	0.043	0.277
Kaolinite	7.91	-	7.83	-0.08	0.248	0.265
	7.91	-	7.82	-0.07	0.240	0.265
Iron	7.89	-	7.81	-0.08	0.265	0.264
	7.90	-	7.81	-0.09	0.264	0.264

*Ionic Strength = 0.02 Molar **k_{DEP} in min^{-1}

A significant difference exists between the rate of ozonation of DEP in phosphate and carbonate buffers (t-test, $\alpha = 0.05$), with the rate less in carbonate. The pH of the buffer solution increased greatly in the case of carbonate.

This phenomena was investigated by ozonation of a pure carbonate solution. In this experiment, an 0.1N solution of sodium bicarbonate was ozonated with an ozone applied dose of 25 mg/L under operating conditions defined in the main body of this report (Table 30). Both alkalinity and pH were followed as a function of time. The pH increased, however total alkalinity remained the same throughout the experiment. There was evidence of high concentration of ozone in solution within 15 seconds. The pH and alkalinity results were as follows:

Time (min)	pH	Total Alk.	Carb. Alk.	Bicarb. Alk.
0	8.32	4870	50	4820
45	9.21	4800	1100	3700

Thus, although total alkalinity did not change substantially throughout this experiment, there was an increase in carbonate alkalinity and decrease in bicarbonate alkalinity on ozonation. Futher investigation will be necessary to determine whether the pH change is a cause or consequence of the carbonate speciation.

An ANOVA analysis of phosphate buffer, kaolinite and iron indicates that these values were significantly different (α =0.05). Although significantly different, the difference is not substantial. Kaolinite slightly decreased the ozonation rate, while iron slightly increased the rate with respect to the ozonation of DEP in a phosphate buffer solution. The change with respect to the phosphate buffer is so small that it would be difficult to optimize these effects in a water treatment situation.

The rate constants predicted by the master rate equation are approximately the same. This is to be expected as the ozone dose was held constant, and the pH nearly maintained as a constant (except for carbonate). In the case of phosphate, kaolinite and iron, the pH decreased slightly, to about the same extent in all three experiments.

Ozonation in Treatment Plant Water

The overall objective of this work was two-fold. The first goal was to investigate the protocol as a rational approach to ozonating micropollutants. The second was to optimize ozonation with respect to a water treatment plant concerned with the removal of micropollutants. Diethylphthalate was ozonated in water samples taken from five treatment locations. These five sites were: untreated Delaware River Water; water from the Rapid Mix which contained ferric chloride and lime; unchlorinated Rapid Sand Filter Influent (RSFI); the chlorinated Rapid Sand Filter Effluent (RSFE); and lastly, ozonated water from the Pilot Plant. The Pilot Plant water was examined to determine the effectiveness of pre-ozonation with respect to reducing interference present in the water which could reduce the rate of ozonation of a micropollutant.

The average ozone applied dose in these experiments was 2.72mg/L. In addition to evaluating the rate of ozonation of DEP, pH, TOC, alkalinity, turbidity, and Ozone Utilized were also measured. The results are presented in Tables E-13, E-14, and E-15.

The differences in the rates of ozonation of DEP in the five water samples were found to be significant (ANOVA, α = 0.05). A significant difference was measured between the measured and predicted values of k_{DEP} for the Delaware River, Rapid Mix, RSFI and RSFE. There is no significant difference between k_{DEP} values for Pilot Plant water (t-tests, α =0.05).

The effect of ozone on pH and alkalinity varied from sample to sample, but generally both pH and alkalinity decreased. There was no significant effect of ozone on turbidity.

The ozone utilized was significantly different for the ozonation of DEP in various all samples. (ANOVA, α =0.05). The untreated Delaware River possessed the highest Ozone Utilized value, and pilot plant water the least.

EFFECT OF WATER MATRIX ON OZONATION PROCESS RATES

TABLE E-13

Sample	pH Before O_3-After O_3	Alkalinity, Before O_3	Alkalinity, After O_3	DOC, mg/L*	Measured $k_{DEP}(min^{-1})$	Predicted $k_{DEP}(min^{-1})$	Difference
Delaware River	7.58 - 7.62	11.6	12.4	2.08	0.170	0.242 ± 0.017	30
	7.59 - 7.64	10.4	15.0	2.08	0.186	0.251 ± 0.017	26
Rapid Mix	7.19 - 6.98	8.2	7.2	ND	0.130	0.210 ± 0.015	38
	7.19 - 6.99	11.8	5.4	ND	0.123	0.210 ± 0.015	41
RSFI	8.56 - 7.51	17.6	13.6	ND	0.194	0.282 ± 0.02	31
	8.54 - 7.42	20.4	13.4	ND	0.181	0.282 ± 0.02	36
RSFE	7.47 - 7.23	16.8	12.4	1.62	0.152	0.229 ± 0.016	34
	7.47 - 7.21	16.6	11.4	1.62	0.153	0.229 ± 0.016	33
Pilot Plant	8.01 - 7.80	31.2	26.8	1.79	0.230	0.269 ± 0.019	14
	8.01 - 7.74	30.8	29.4	1.79	0.215	0.267 ± 0.019	20

*DOC, Dissolved Organic Carbon; for water sample w/o DEP these values are monthly composites from the Philadelphia Water Department.

** Alkalinity as mg/L $CaCO_3$

ND = Not Determined

TABLE E-14. OZONE UTILIZED

SAMPLE	OZONE UTILIZED
	mg O_3/liter solution
Delaware River, w/DEP	13.8 ± 1.12
Rapid Mix, w/DEP	13.00 ± 0.86
RSFI, w/DEP	11.33 ± 1.23
RSFE, w/DEP	12.7 ± 0.85
Pilot Plant, w/DEP	9.64 ± 1.89
Delaware River alone	5.52 ± 1.03
pH 8 phosphate, w/DEP	5.80 ± 1.51

TABLE E-15. TURBIDITY

SAMPLE	BEFORE O_3, NTU	AFTER O_3, NTU
Delaware River	23	22
Rapid Mix	24	23
RSFI	3	ND
RSFE	0.16	0.16
Pilot Plant	0.09	0.08

ND = Not Determined

River. The value for the pilot plant water is about half this value, or 17%

rates is about 35% for all the Torresdale water samples and the Delaware River. The value for the pilot plant water is about half this value, or 17% less.

In terms of optimizing the ozonation process for DEP removal, ozone should be applied prior to rapid sand filtration and prior to the post chlorination step. In the processed waters examined, the rate of DEP removal was fastest in RSFI. This was attributed to the high pH and low turbidity of this water sample.

Besides yielding the fastest ozonation rate, RSFI is also partially purified with respect to removal of humics, particulates, colloidal organics and micropollutants found in raw Delaware River water. Many micropollutants, including phthalate esters, are probably partially removed by conventional coagulation and sedimentation. Humic materials and particulates are well removed by conventional water treatment processes (E-12). Potentially, ozonating prior to RSFI would utilize ozone as a clean up step to remove micropollutants not completely removed by conventional treatment. This could further enhance the quality of a particular water supply for human consumption.

As an alternative to ozonating prior to rapid sand filtration, the untreated Delaware River water would be the second choice for the application of ozone. The rate of removal of DEP was only slightly slower in the river than in RSFI. Ozonating the Delaware directly would lack the potential as a clean up step for conventional coagulation and sedimentation. Previously it has been demonstrated that, with respect to TOC and UV removal, ozonating a raw water supply is superior to ozonating partially treated water (see above). This has not been demonstrated for micropollutant removal, only for the non specific parameters of TOC and UV or ozone demand causing substances. The current research indicates that ozonating the rapid sand filter influent is slightly superior to ozonating raw river water in terms of micropollutant removal.

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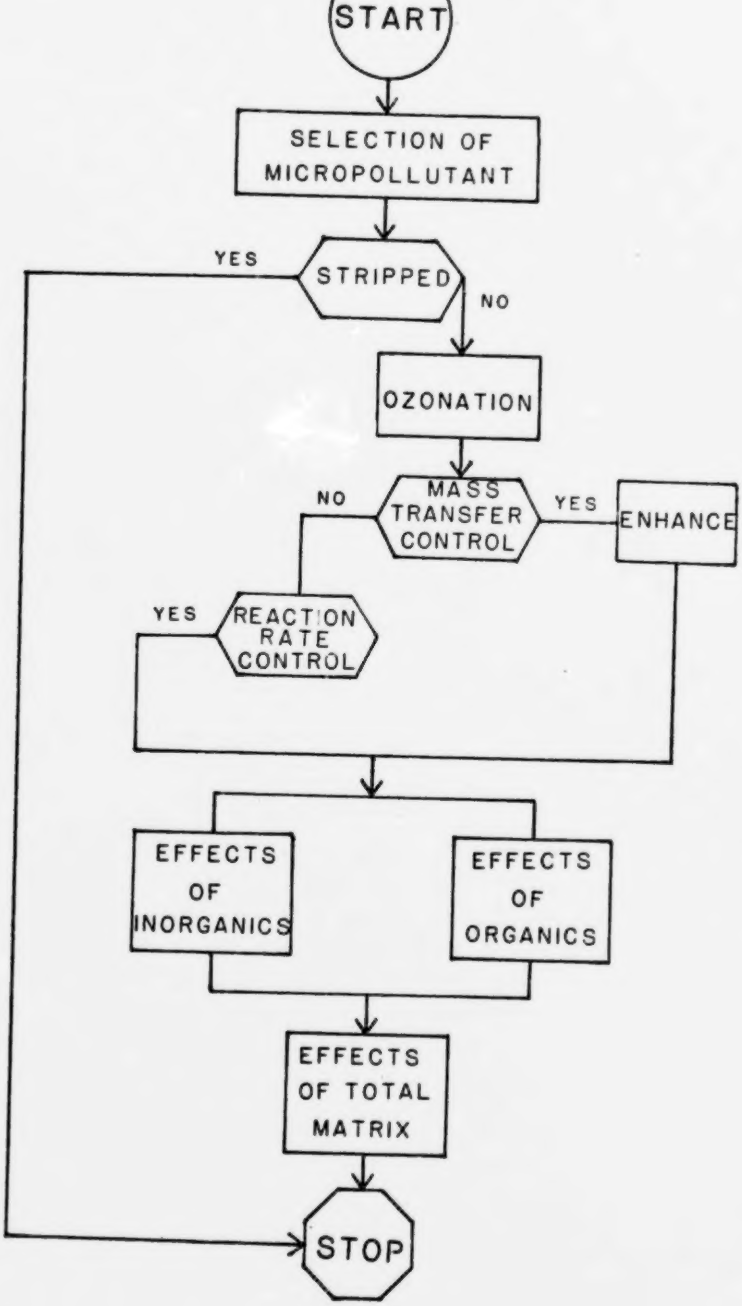
START
SELECTION OF MICROPOLLUTANT
STRIPPED
YES
NO
OZONATION
MASS TRANSFER CONTROL
NO
YES
ENHANCE
REACTION RATE CONTROL
YES
EFFECTS OF INORGANICS
EFFECTS OF ORGANICS
EFFECTS OF TOTAL MATRIX
STOP

Figure E-1 Micropollutant protocol flow scheme.

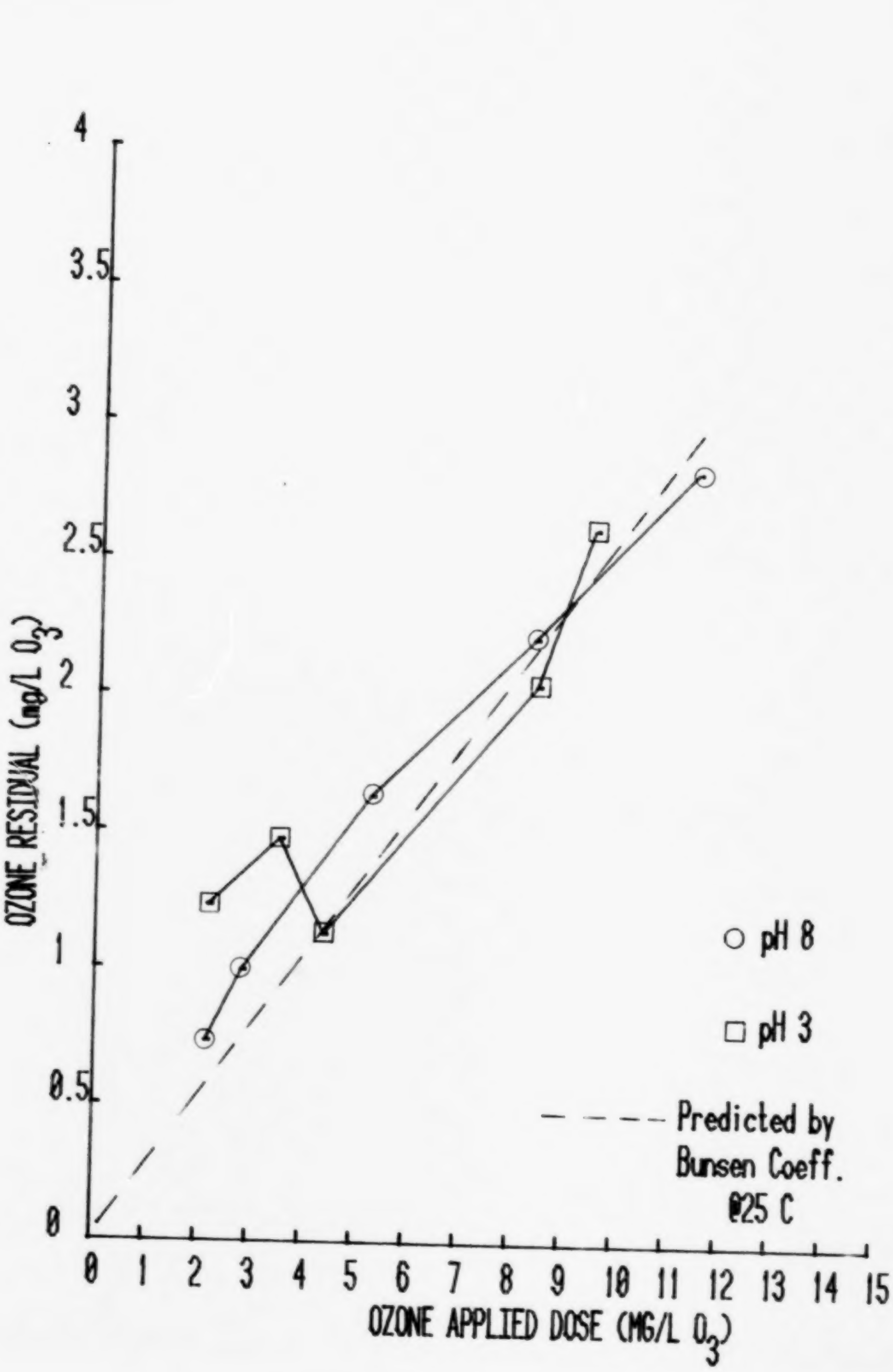

Figure E-2 Bunsen coefficient as a predictor of ozone saturation concentration.

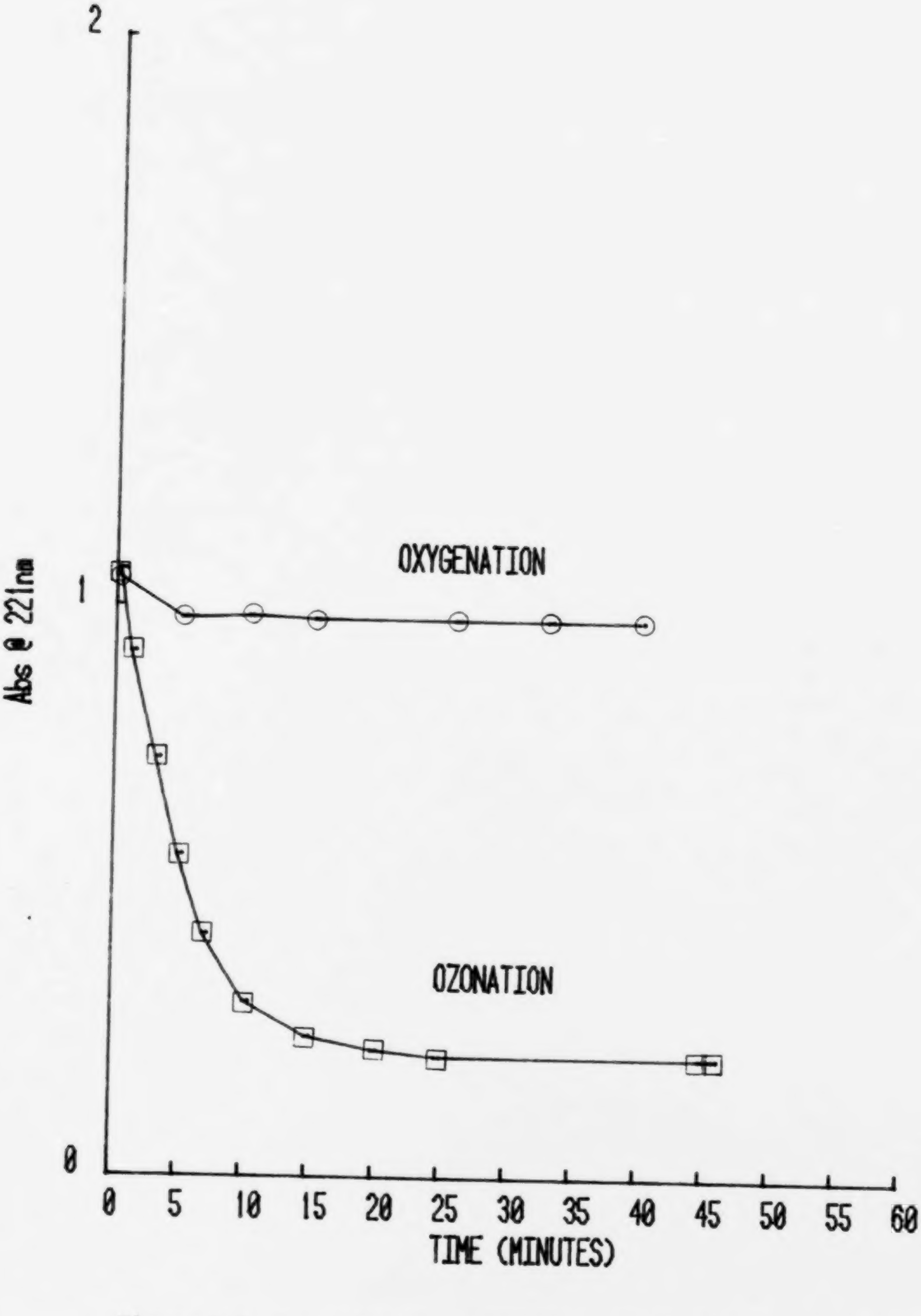

Figure E-3 Ozonation vs. Oxygenation of diethyl phthalate.

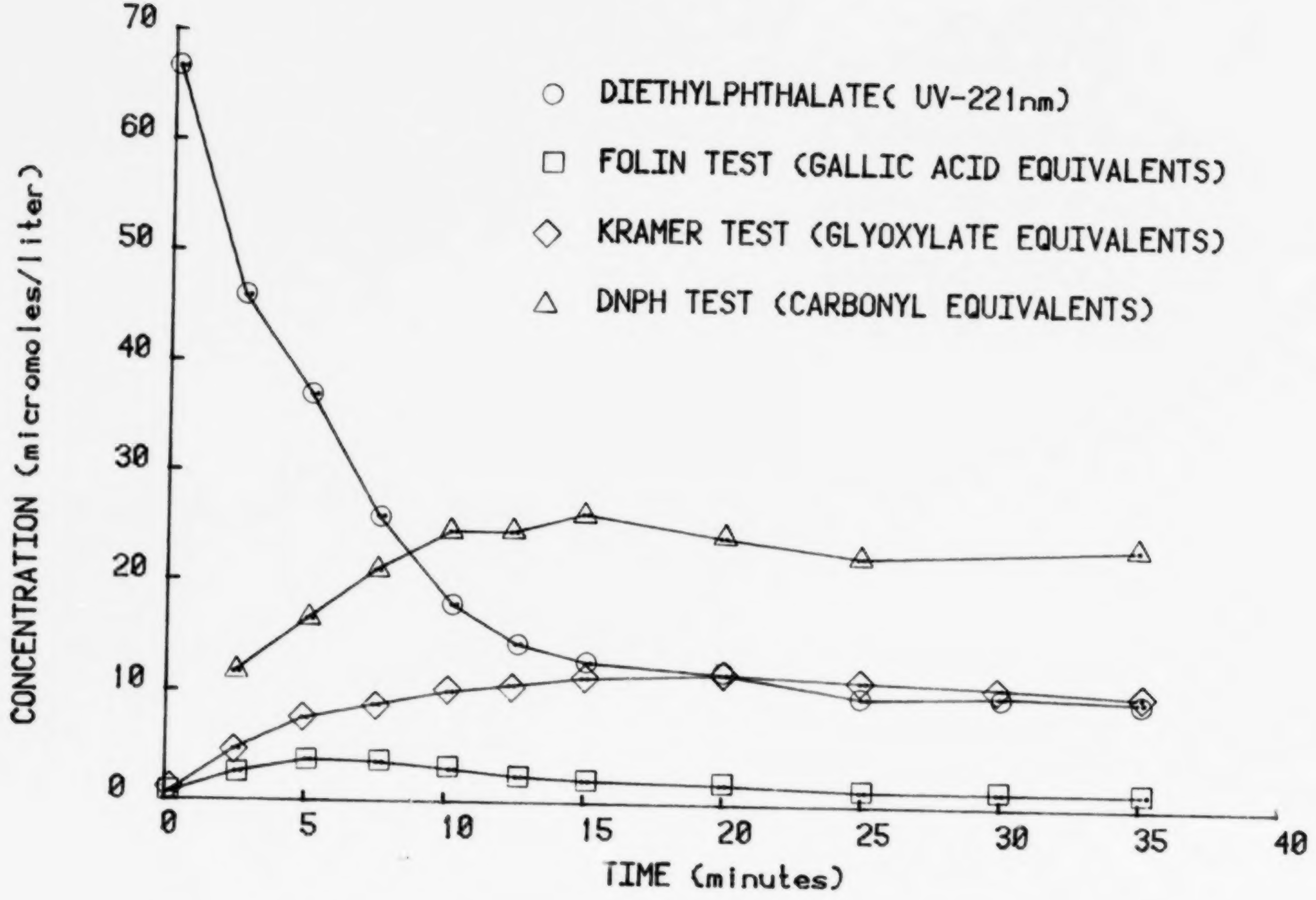

Figure E-4 Products of ozonation of diethyl phthalate at pH 8.

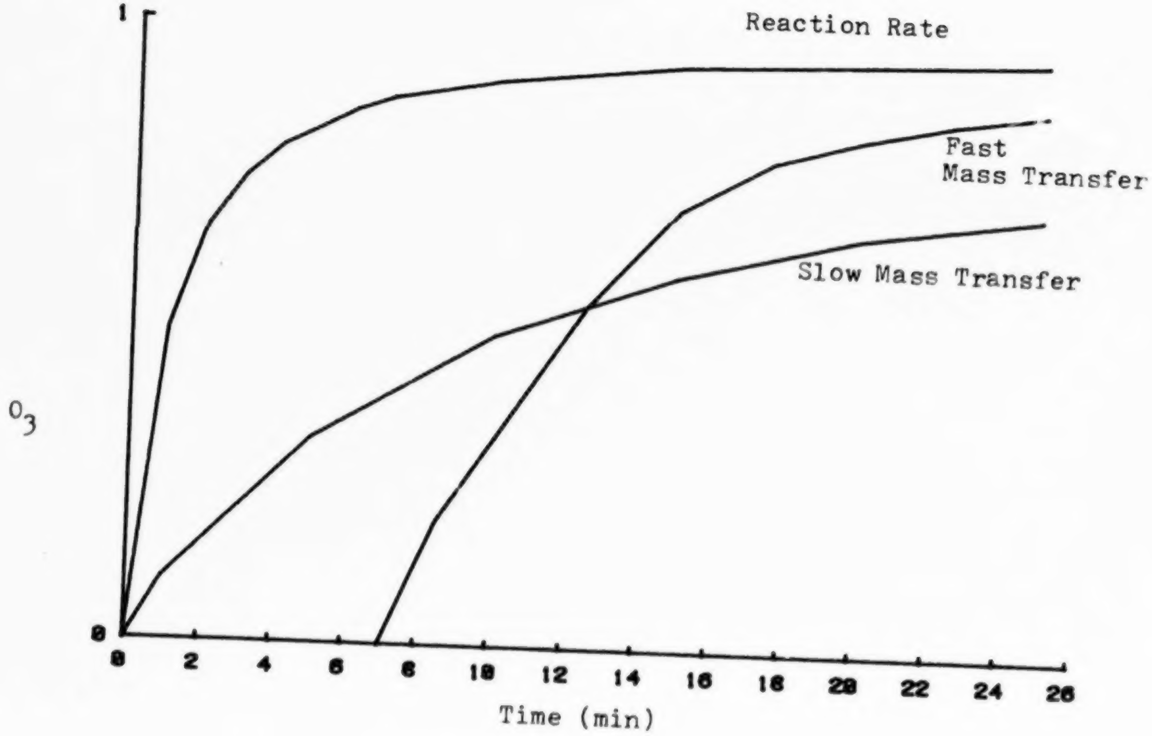

Figure E-5 Theoretical mechanisms of ozone uptake.

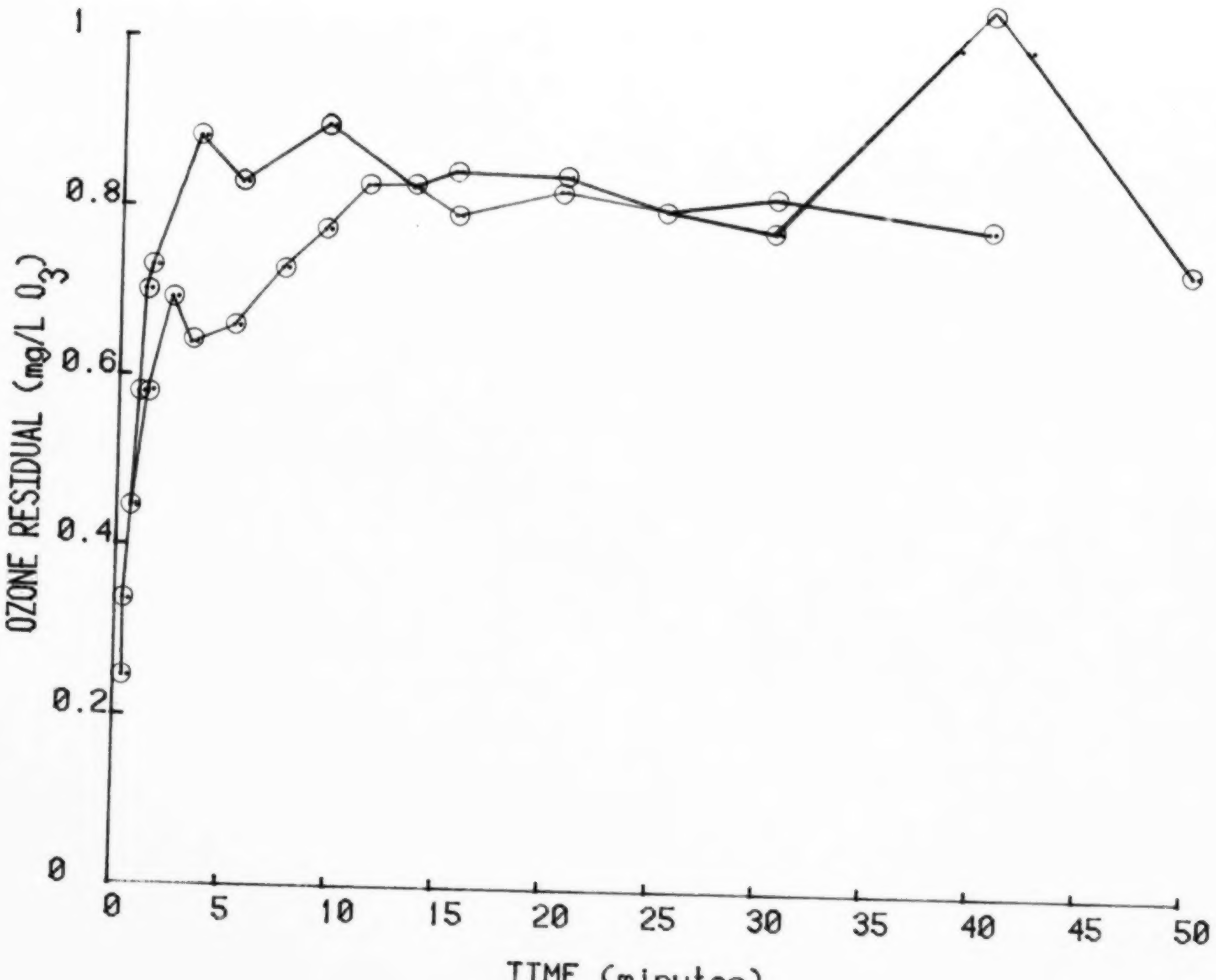

Figure E-6 Diethyl Phthalate: Ozone uptake at pH 3.

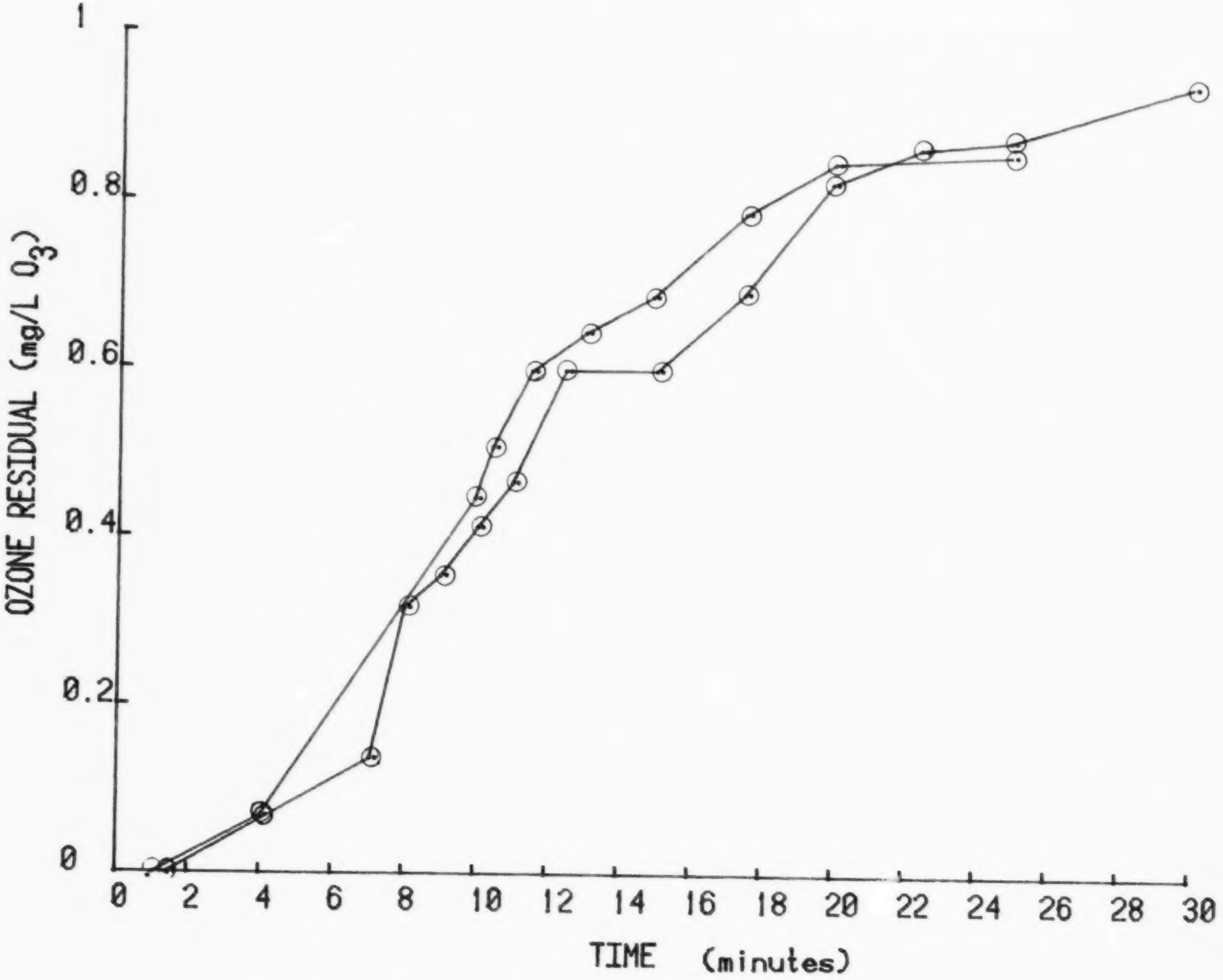

Figure E-7 Diethyl Phthalate: ozone uptake at pH 8.

APPENDIX F

BROAD SPECTRUM ANALYSIS OF MINI-COLUMNS

INTRODUCTION

This appendix presents analysis of samples collected on macroreticular resin accumulators during the first 18 weeks of the mini-column study. This encompasses the adsorption reproducibility study and a portion of the long term study. Details of the mini-column operation are given in the main body of the report. The major differences between the specific organic analysis used in the pilot and main plant, and the methods used in the mini-column study lie in the design of the resin accumulator, the elution technique, and the use of packed column GC analysis of the samples as a preliminary screening technique. The differences are summarized below:

	Pilot and Main Plant	Mini-columns
Sampler Design	750 mm x 50 mm	250 mm x 40 mm
Resin Volume	100 ml	140 ml
Elution Technique	3 elutions (150, 100, 100 ml)	4 elutions (100 ml each)

These differences resulted from the use of teflon segmented columns for samplers in the mini-column experiments. These samplers had insufficient volume to allow the initial 150 ml ether elution.

This appendix also includes carbon core analysis not included in the pilot or main plant experiments. Carbon core analysis was made possible through the column breakdown study, but was discontinued after nine weeks. The operation of the contactors from which experimental samples were taken is summarized below:

Mode	Column #	Date of Operation	Weeks	Comments
Ambient (24° - 30°C)	1 - 8	6/2/80 - 7/23/80	7	Columns 1 to 4 were taken off line at two week intervals

Ambient (warm) (15° - 31°C)	5,8	7/23/80 - 10/17/80	8-18	Column 5 taken off line at week 9
Chilled (cold) (6° - 17°C)	6,7	7/23/80 - 10/17/80	8-18	Column 6 taken off line at week 9

The results of the G.C. profile screening method were difficult to interpret without making subjective judgments and were very time consuming; thus, a new statistical approach for interpreting G.C. profiles was developed (F-1). This new evaluation method for broad spectrum analysis utilizes Chi-square contingency tables and is capable of determining, statistically, the differences between capillary G.C. chromatograms of 200-300 peaks. This method was used in the present study to characterize the GAC adsorption process with respect to the:

(1) Reproducibility of removal of trace organics by GAC contactors

(2) Temporal variability of the influent to the GAC contactors

(3) Spatial variability of the influents vs the effluents of GAC contactors

(4) Spatial location of the trace organics on the GAC columns from analysis of cores of carbon from the contactors

(5) The effect of temperature on the removal of trace organics by GAC contactors

(6) Selection of samples for GC/MS analysis where significant differences between capillary chromatograms are observed.

EXPERIMENTAL

GC Profile Analysis

This study was conducted over a period of 18 weeks from June 1, 1980 to October 17, 1980. Samples were taken after ozonation (ozone dose - 1.2 mg/l and contact time of 30 minutes) and after carbon filtration (15 minutes contact time). Each sample represents the extraction of $\approx$ 340 L of water by an XAD2 macroreticular resin (MRR) accumulator at a pH of 2 and at the temperature of the GAC contactors sampled. The resins were eluted with 4 x 100 ml of ether. The ether was dried with Na_2SO_4 and concentrated to one ml by two step Kuderna-Danish evaporation. The resultant one ml samples were base extracted using a pH 12 potassium carbonate/ potassium hydroxide solution (F-2).

The samples were then chromatographed on a 60 meter 0.21 mm i.d. bonded phase SE 30 fused silica, capillary column using a Carlo Erba Model 2050 chromatograph. The samples were analyzed by cold trapping on the G.C. at < 40°C for 2 minutes, a ballistic rise to 50°C, 50°C isothermal operation for

3 minutes and then programming to 260°C at 3.5°C/min for a run time of 65 minutes. The retention times and peak areas of the chromatograms were then entered into a Tektronix 4051 computer where the chromatograms were reconstructed and statistically analyzed. Selected samples were further analyzed by GC/MS. Chromatographic response was plotted on a logarithmic scale from (1E -3 to 1E) to facilitate a semi-quantitative order of magnitude comparison of the data. This represents an aqueous concentration range of 0.3 - 3,000 ng/l and assumes 100% recovery.

Chi-Square Analysis

The Chi-square analysis is a non-parametric, enumeration statistical method (F-3). It is one of the simplest methods of pattern recognition, relying on frequencies or counts in specific classes or categories examined. Chi-square analysis is defined by equation (F-1)

$$\chi^2 = \sum \frac{(f_i - F_i)^2}{F_i} \qquad \text{(C-1)}$$

where f_i is the observed frequency in class i and F_i is the expected (theoretical) frequency in class i.

The method used here is a 4 x 4 contingency table test for homogeneity. The calculation is performed by dividing each chromatogram into four time sections (these are the columns, see Figure F-1) and two area sections (these are the rows, see Figure F-2). Each chromatogram, then, is divided into eight sections. The Chi-square analysis evaluates two chromatograms at one time, for a total of 16 sections (4 x 4 table). The expected or theoretical frequency is calculated by multiplying the sum of the column and the row in which the observed frequency of interest is located and then dividing the above by the total observed frequency.

The null hypothesis tested is

H_O - the two chromatograms are from the same population (i.e. they are homogeneous)

H_A - the two chromatograms are not from the same population (i.e. they are heterogeneous or different).

This test is performed at the 95% confidence level with nine degrees of freedom.

RESULTS & DISCUSSION

Reproducibility

The evaluation of the reproducibility of the adsorptive process was performed using replicate GAC contactors and replicate XAD-2 MRR accumulators. Three statistical approaches were used to evaluate the gas chromatographic output.

The first approach was a simple statistical analysis of the two normal alkanes (F-12 and F-18) added as the internal standards. The retention times (absolute and relative) and the areas (absolute and relative) of F-12 and F-18 were evaluated for deviations from their respective means (standard deviation). The results are presented in Table F-1 and show that the relative retention time and the relative area for the standards is precise (low % standard deviation). This indicated that the G.C. procedure was reproducible throughout the analysis period.

The second approach was to use the Chi-square analysis on replicate samples. This was carried out using 4 x 4 contingency tables as previously described. The Chi-square analysis indicated that, at the 95% confidence level, replicate effluents were homogeneous. The GAC process, then, is assumed to be reproducible, since columns with identical influents are shown to have homogeneous effluents.

The third approach was to use a student t-test to evaluate replicate samples. Here, sixteen peaks were chosen at random from the G.C. profile of the effluent from GAC column 4, week 7. These peaks became the reference peaks for the student t-test evaluation. Each of these peaks were found (by their relative retention times) in the other effluent chromatograms and their relative areas were recorded. When comparing two chromatograms, the area of each reference peak from one chromatogram was subtracted from the area of the corresponding reference peak in the other chromatogram. These differences were then tested, by the use of the student t-test, to see if the mean of these differences differed significantly from zero. The null hypothesis tested is that the mean of the differences of replicate effluent reference peaks is not significantly different from zero. This was done at a 95% confidence level. It was not possible to reject the null hypothesis for any of the replicate effluent cases.

Replicate effluents did not differ from one another at $P = 0.05$ by any method of analysis. The statistical findings, as well as the raw chromatograms, indicate that replicate effluents are similar. Thus, the adsorption process, as analysed, is reproducible for a broad spectrum of nonpolar organic compounds.

Influents to the GAC contactors

Figure F-3 shows the complex capillary G.C. profiles of the influents to the GAC contactors for weeks 3, 4, and 5. Figure F-4 shows the capillary G.C. profiles of the influents for weeks 10, 11.5 and 13. The traditional peak by peak interchromatogram area comparisons for the evaluations of these G.C. profiles is too cumbersome; therefore, the Chi-square statistical analysis was performed.

Using Chi-square contingency tables to understand ten sets of complex influent chromatograms resulted in the observation that the influents for weeks 3, 4 and 5 were not homogenous at $P = 0.05$ (Figure F-3). The major differences between these chromatograms occurred in the first (0-17 min) and third (31-54 min) time divisions. The remainder of the influent chromatograms were not different enough by Chi-square to reject the null hypothesis

(H_o - samples are homogenous) at the 95% confidence level (Figure F-4).

The chromatograms for which Chi-square analysis showed significant differences appeared different by visual inspection (Figure F-3). However, some visual differences were also observed between chromatograms for which the Chi-square analysis did not show any significant differences (Figure F-4). This points out that the Chi-square is only a first step in analyzing complex chromatographic data. Further statistical analysis as well as direct peak to peak comparisons must eventually be performed. The Chi-square analysis points to the chromatograms and areas of chromatograms which are potentially most important for further evaluation by GC/MS.

Table F-2 shows the compounds tentatively identified by GC/MS analysis in this study. Figures F-3 & F-4 assign tentative peak identifications to G.C. profiles of influents according to retention time data from influent week 9 which has undergone GC/MS analysis. A number of trihalomethanes (THMs) are present in the influent water to the GAC contactors even though there was no chlorine added during the pilot plant treatment train. This indicates that some THMs come into the treatment plant from the Delaware River and are not formed by a treatment plant process. There are also a number of other compounds of potential health concern observed in the influent water. These include: bis(2-chloroethyl)ether (a priority pollutant), a triazine, an atrazine, and chlorinated nitrobenzenes. Most of these compounds and a couple of other low MW chlorinated compounds also have been identified on the GAC cores by GC/MS. Thus an independent technique of isolation has confirmed the existence of those compounds isolated by XAD-2 resin from the influent water. Previous pilot studies at the Torresdale drinking water plant on the Delaware River have also identified many of the compounds (F-4) in Table F-2.

Effluents from GAC Columns

Figure F-5 shows the capillary GC profiles of the effluent samples from weeks 11.5, 13 and 18. These chromatograms show fewer GC peaks than the influents indicating that the GAC contactors are adsorbing numerous compounds. The effluents have, generally, between 100-200 fewer peaks than the influents for the 18 week run. Analysis by GC/MS was performed on a select number of effluents. Tentative identifications are listed in Table F-2 and on Figure F-5 for week 18. It is interesting to note that there were no chlorinated organics identified by GC/MS in any effluent sample from this study. It should also be noted that a number of the compounds which were tentatively indentified are suspected contaminants from the XAD-2 MRR accumulators (F-5). These possible contaminants were observed in the influent and effluent resin analyses but not on the CH_2Cl_2 -carbon core extracts.

When Chi-square analysis was performed on the effluents from the GAC contactors, the results indicated that for the first 11.5 weeks of the mini-column run the effluents were homogeneous at $P = 0.05$. Figure F-6 shows few peaks changing an order of magnitude in response. The large number of peaks at the end of the effluent chromatograms for week 3 and 5 are suspected laboratory contaminants. The last two sampling periods were not homogeneous at $P = 0.05$ (Figure F-5 - weeks 13 and 18). These samples will be considered further in the next section.

Warmed Vs Cooled Influent Water - Weeks 8-18

On 7/28/80, eight weeks into the GAC run, the influent water to two GAC contactors was dropped approximately 15°C while the influent water to the two remaining contactors was not changed. The chromatograms of the effluents for the next 4 weeks (up to week 11.5) did not show any statistical difference at $P=0.05$ by the Chi-square analysis. It was not until week 13 that a statistical difference in the effluent from the cold contactor was determined at $P = 0.05$ (Figure F-5). The effluents from the cold contactor for weeks 13 and 18, are different from each other as well as from previous warm and cold contactor effluents.

Figure F-7 is a comparsion between the warm contactor effluent and the cooled contactor effluent. It is visually quite apparent, as well as statistically significant at $P = 0.05$, that these two effluent chromatograms are different, especially in the middle section of the chromatogram between F-12 and F-18. The peaks marked with * represent peaks decreasing in intensity by an order of magnitude or more from warm to cold while those marked with * are peaks which increased in intensity by more than an order of magnitude from warm to cold. Most of these compounds were not identified by GC/MS analysis on the first trial and are undergoing more rigorous GC/MS investigation.

The interpretation of the differences between the effluents of the warm contactors and the cold contactor relies on the contactors having equivalent histories and being homogeneous until the temperature change. When peaks are observed to change in intensity in the effluents, any or all of the following mechanisms may be at work:

(1) reequilibration of the adsorbed substrate to a cooler influent, although the influents had been cold for 5 weeks before any difference between warm and cold contactors were noticed.

(2) kinetically limited removal in the cooler contactor, although investigations of TOC during this work have not seen this change (F-6).

(3) decrease in bacterial removal from the cooler water stream.

(4) differences in the temperature of the resin collectors resulting in different extracts; however, temperature has been shown to have minimal effects on other solid adsorbants (F-7).

The observed differences are important since the most efficient design for a GAC contactor relies on understanding the underlying removal mechanism(s).

Analysis of Carbon Cores

The chromatographic results of extracting the adsorbed organics from the carbon surface are shown in Figure F-8. These are packed column GC profile analyses of each of 3 sections (top, middle, and bottom) of GAC columns between week 1-9. It can be seen that the majority of the components which are extractable into CH_2Cl_2 are found on the top section of each column. In only one instance does a significant amount of extractable material appear on any but the tops of the columns and that is on the extract of the middle of column 6 (the cold column for week 9). This seems consistent since displacement of adsorbed compounds from the top of the contactor and their readsorption deeper in the bed would result in no observed effluent differences. This agrees with the previously described effluent analysis.

When the top of the column extracts are shown together in the capillary profiles of Figure F-9, it can be seen that some compounds are accumulating with time and some are decreasing with time. Those peaks marked with an * are increasing with time and the peak marked with a * is decreasing with time. The majority of peaks, however, are not changing with time. These peaks represent compounds which are apparently at equilibrium with the influent water and the GAC at the top of the contactor. They are still being removed before the bottom section of the contactor which was sampled and showed little accumulation of extractable compounds.

Figure F-10 shows the comparison between the CH_2Cl_2 extracts of organic compounds from the GAC cores at the top of the warm contactor and the cold contactor after week 9. These two contactors were sampled at approximately the same time. Chi-square analysis has shown these samples to be significantly different. There are many compounds which show an increased surface concentration on the cold contactor as compared to the warm contactor. This agrees with earlier observations of more rapid breakthrough of some compounds from the cold contactor. The compounds which are increasing in intensity from the warm contactor to the cold contactor may represent compounds which are:

1. (1) better adsorbed at lower temperatures.
2. (2) not being removed as effectively from the water stream or displaced from the top of GAC column in the cooled contactor as compared to the warmed contactor.
3. (3) varying only due to analytical error. There is no measure for reproducibility of the CH_2Cl_2 extraction as there was with the method used for analyzing the effluents.
4. (4) biologically removed.

Summary

This paper has used Chi-square contingency tables to determine differences between capillary GC chromatograms of 200-300 peaks. This method determined the significant differences at $P = 0.05$ between capillary GC chromatograms of 3-day composite samples of weekly influents and effluents (temporal changes) influent vs. effluents of GAC columns (spatial changes); spatial location of trace organics on GAC columns; and differential temperature on the removal of trace organics by GAC contactors.

Specific conclusions related to the removal of trace organics in an ozone-GAC potable water pilot plant study are:

(1) Replicate carbon contactors had reproducible effluent GC profiles. This should be studied more rigorously and may depend on source water homogeneity and the length of time the con tactor has been on-line.

(2) The influents to the GAC columns for weeks 3, 4, and 5 showed variability after which the influents were homogeneous (weeks 6-8). The time windows in which the greatest contribution to the overall chi-square occurred were 0-17 minutes and 31-45 minutes.

(3) The effluents for weeks 3 - 11.5 were homogeneous.

(4) The effluents of the cooled contactor for weeks 13 and 18 differed from previous effluents, each other, and the warm contactor effluents. This study indicates that GAC contactors may behave differently at different temperatures for the removal of trace organic compounds. This may become an important consideration in areas where source water varies significantly in temperature.

(5) GAC core samples from week 9 showed differences between the cooled contactor and the warm contactor.

(6) A number of chlorinated organics were observed in the influent to the GAC contactors. Most of the chlorinated organics observed in the influents to the GAC contactors were observed on the surface of the GAC. No chlorinated organics were identified in the effluents by GC/MS analysis during this 18 week study.

TABLE F-1. STATISTICAL EVALUATION OF STANDARDS

INF/EFF	RETENTION TIME	% STANDARD DEV. RETENTION TIME	% STANDARD DEV. RESPONSE
C-12	26.12 + 0.08	0.3	37.1
C-18	47.91 + 0.1	0.2	35.4

RELATIVE RETENTION TIME (R.T. C-18/ R.T. C-12)	% STANDARD DEV. RELATIVE RETENTION TIME (1σ)
1.83 ± 0.002	0.1

RELATIVE RESPONSE (RESP. C-12/ RESP. C-18)	% STANDARD DEV. RELATIVE RESPONSE (1σ)
2.46 ± 0.18	7.5

TABLE F-2. THE IDENTIFICATION OF COMPOUNDS TENTATIVELY IDENTIFIED^a BY GC/MS ANALYSIS IN THIS STUDY

	-8/4/80- Effluent O_3 Pilot Plant, Influent to GAC Mini Columns Week 9	-10/17/80- Effluent GAC Mini Columns Week 18	GAC Cores Week 10
A. Aromatic			
1. C2-Benzene is		X	X
2. C3-Benzene is		X	X
3. Acetophenone		X	X
4. C2-Benzaldehyde is	2	1	
5. C2-Acetophenone is	2	2	
6. Methyl benzoate	X^b	X^b	
7. C2-methyl benzoate is	2	2	
8. Methyl sulfonyl benzene			X
9. C2-Phenol isomer		1	
10. Ethyl benzoate		X	
C. Chlorinated Organics			
1. Dibromochloromethane	X		X
2. Bis(2-chloroethyl) ether	X		X
3. Dichlorobenzene is	1		
4. 1,2-Bis(2-chloroethoxy) ethane	X		X
5. Dichlorobromomethane	X		X
6. Tetrachloroethylene			X
7. 1,2-Dichloropropane			X
8. Bromoform			X
9. Chloronitrobenzene is	X		
10. Dichloronitrobenzene is	X		
11. Atrazine	X		X
12. 2,4 Bis(ethylamino)-6-Chloro-s-triazine	X		
13. Lindane	X		
M. Miscellaneous			
1. Ethyl acetate	X	X	
2. 1, 2:3,4-L-arabinopyranose			X
3. 1, 2:3,5-D-xylofuranose	X		X
4. 2, 3:4,6-L-sorbofuranose	X		X
5. Tributyl phosphate	X		X
6. 2,3:4,5-D-fructopyranose			X
7. Dihydroactinidiolide	X		X
8. Fatty Acid Methyl Ester	5	6	
9. Phthalate Ester	2	3	3

		-8/4/80- Effluent O_3 Pilot Plant, Influent to GAC Mini Columns Week 9	-10/17/80- Effluent GAC Mini Columns Week 18	GAC Cores Week 10
10.	n-C9 HC		X	
11.	n-C10 HC		X	
12.	n-C11 HC		X	
13.	Diphenyl Ether			X
14.	Di acetone Sugar isomer related to M.2-4, 6	6	12	

[a] Tentatively Identified - Observed by matching mass spectra and library mass spectra

[b] Observed in blank

is = Isomer

HC = hydrocarbon

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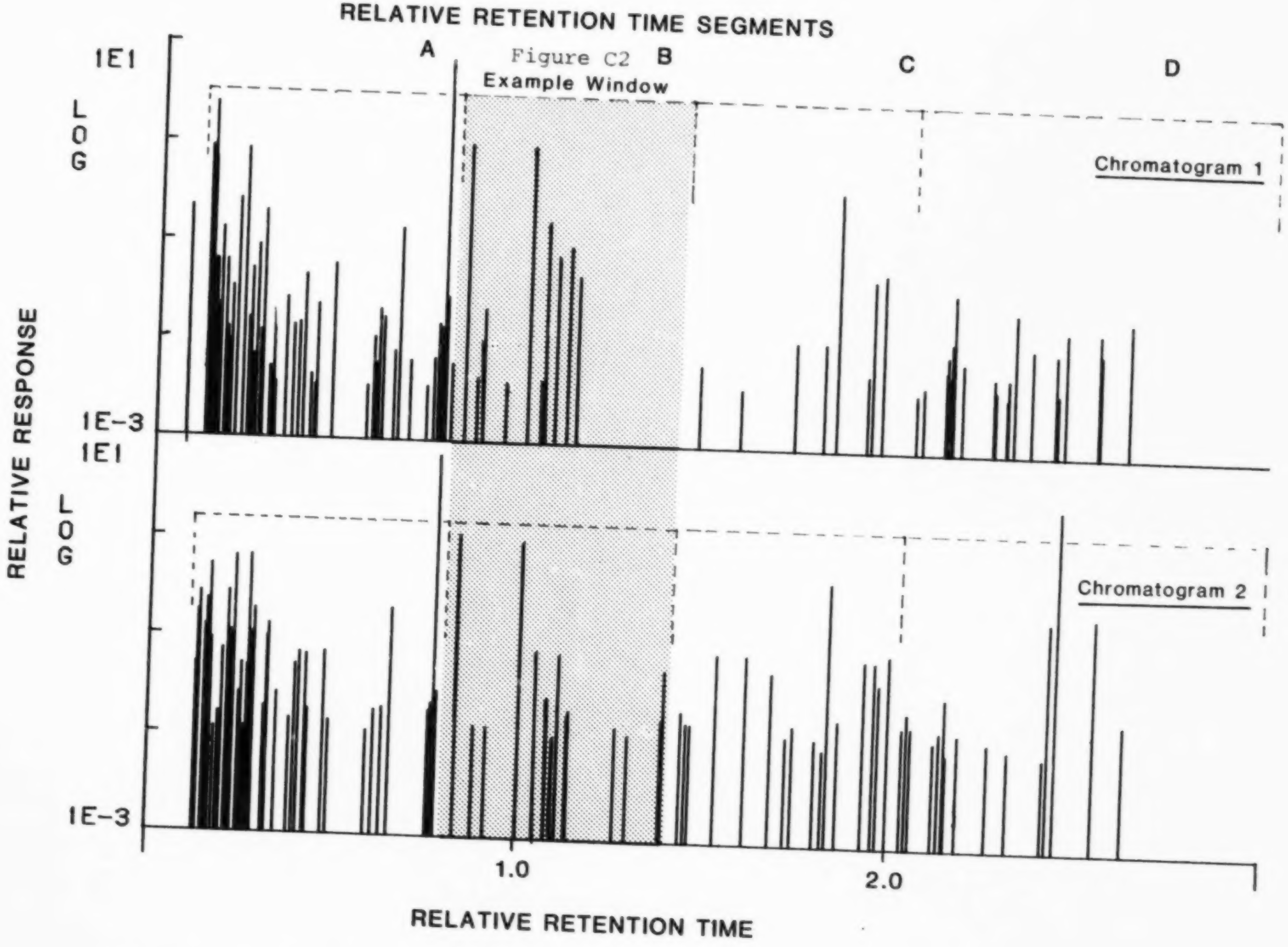

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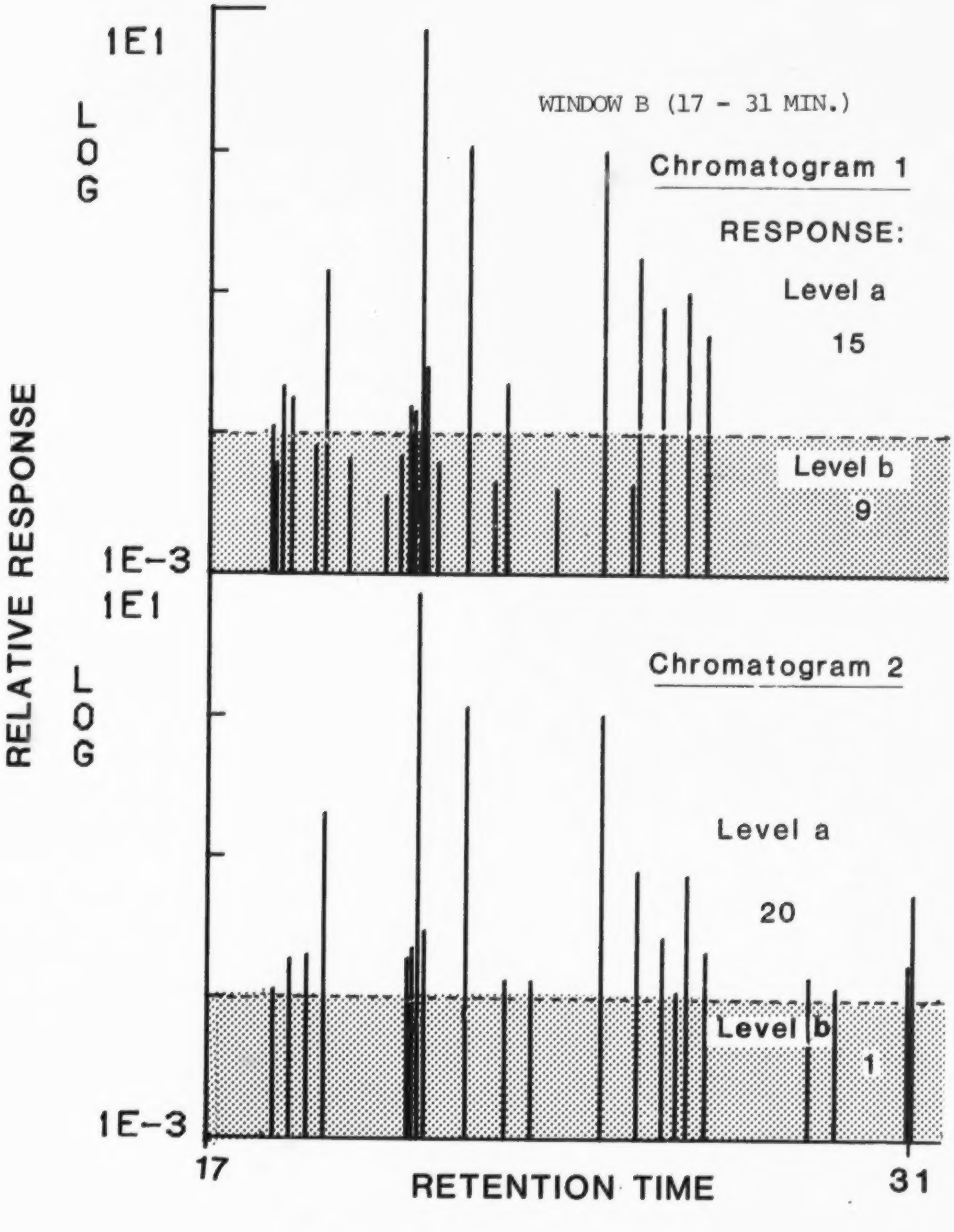
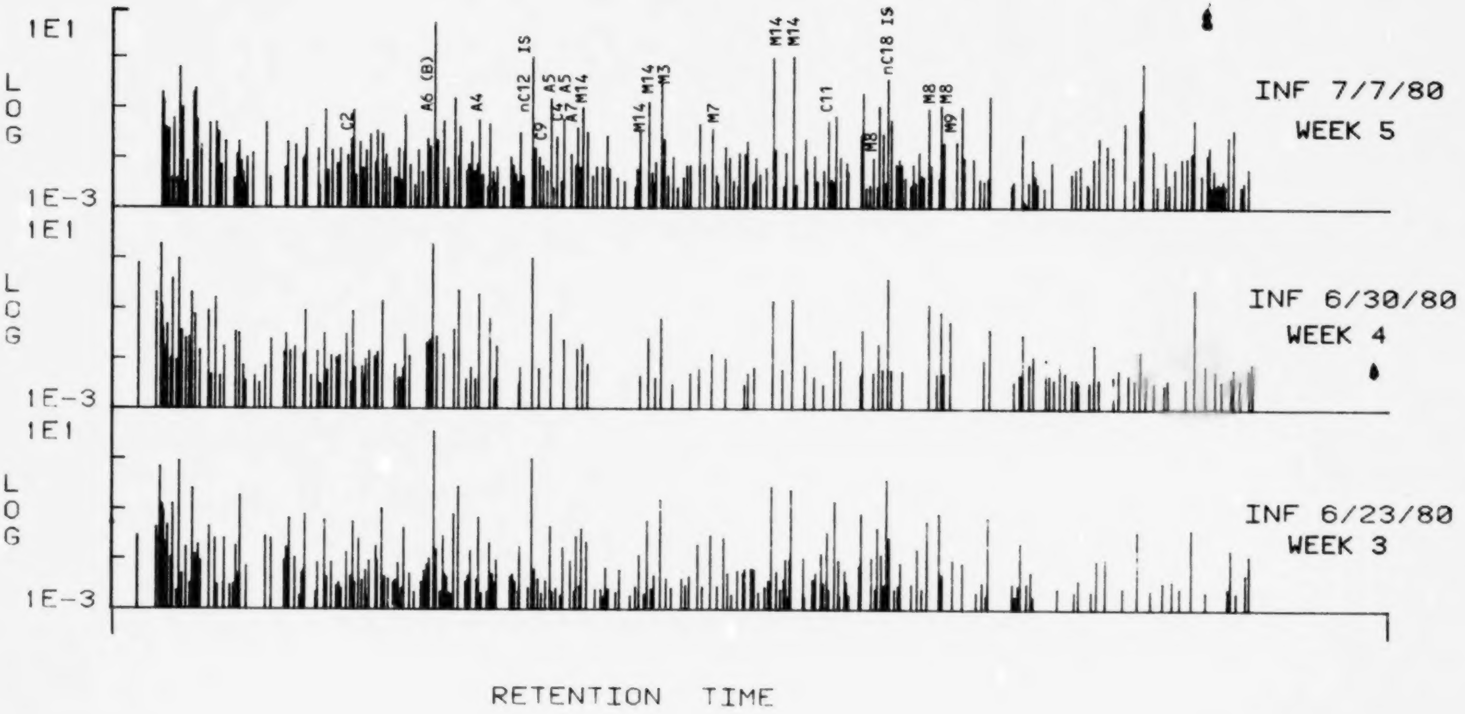


Figure F-2 Example of the breakup of each time category into two area categories for Chi Square Analysis; 1. Above 3 ng/, and 2. Below 3 ng/.



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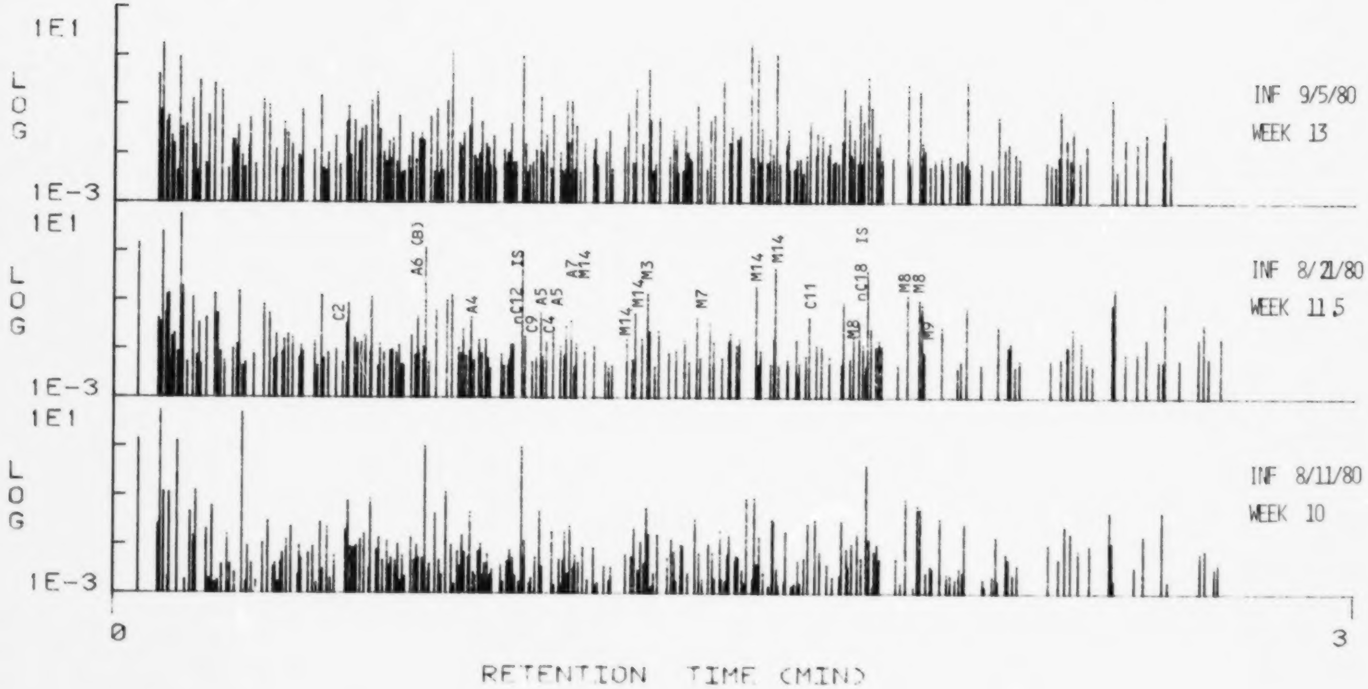
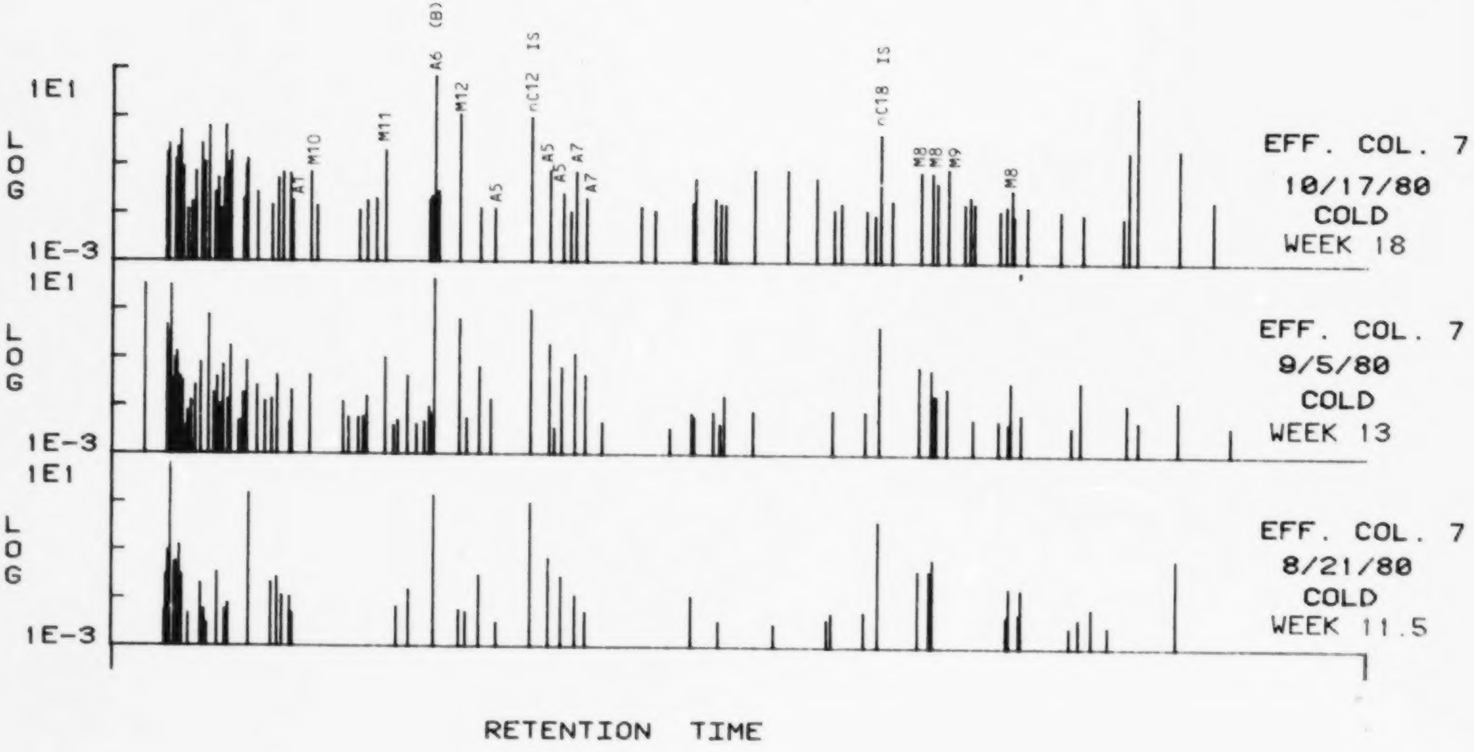


Figure F-4 Influent chromatograms from weeks 10, 11.5 and 13 to show; 1. Influent complexity, 2. Homogenous influents and 3. GC/MS tentative identification as determined by the similarity of the GC peak retention times compared to the influent sample of week 9.



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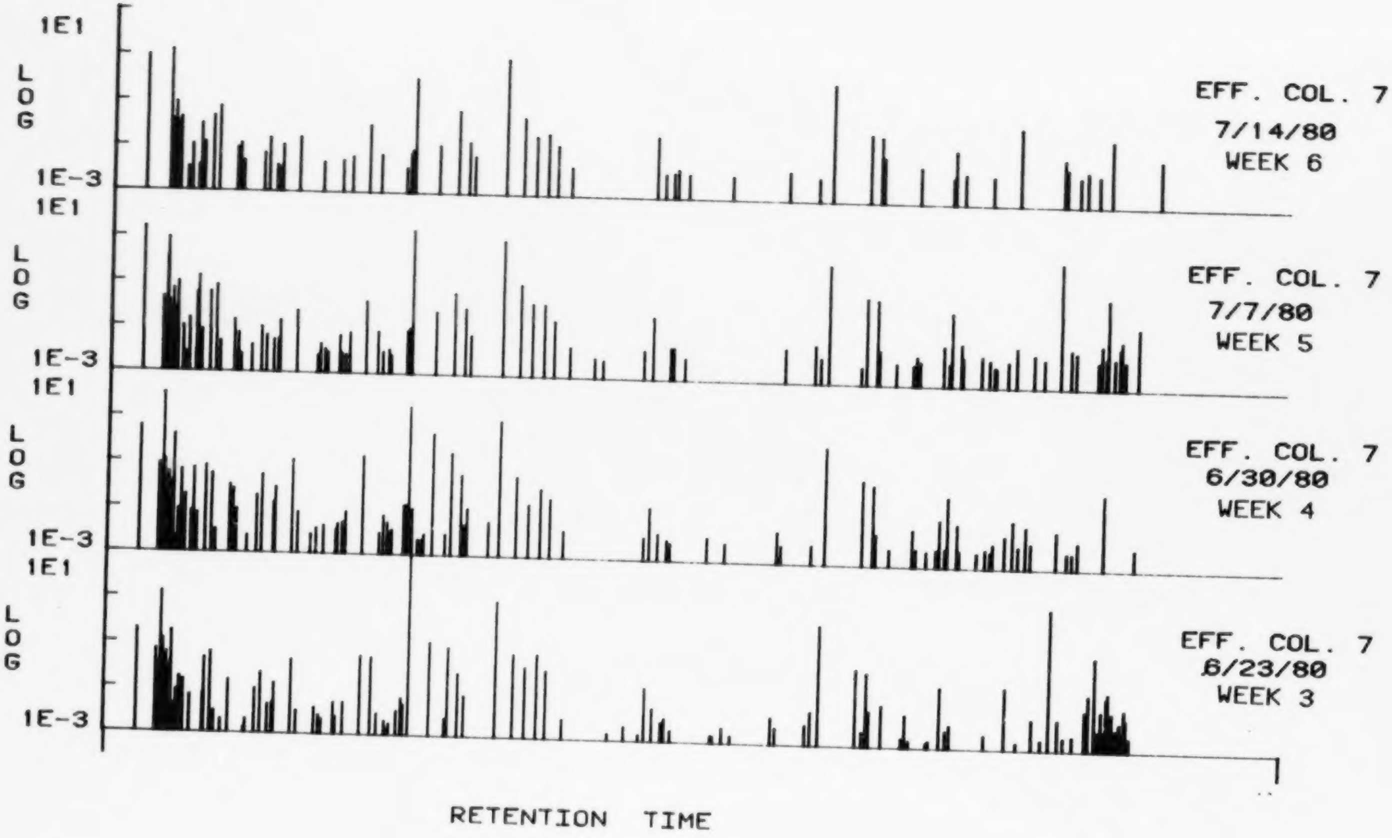

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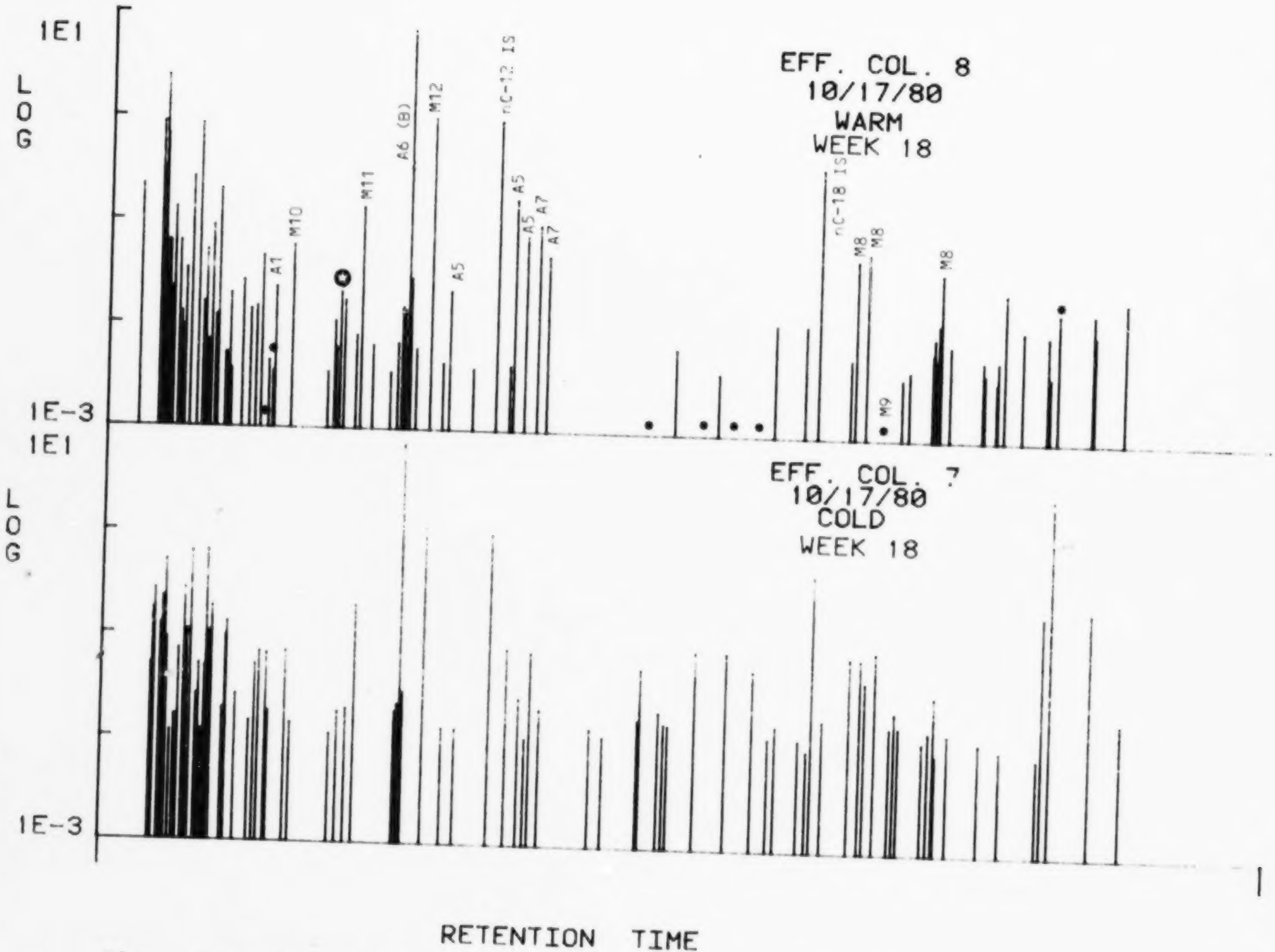

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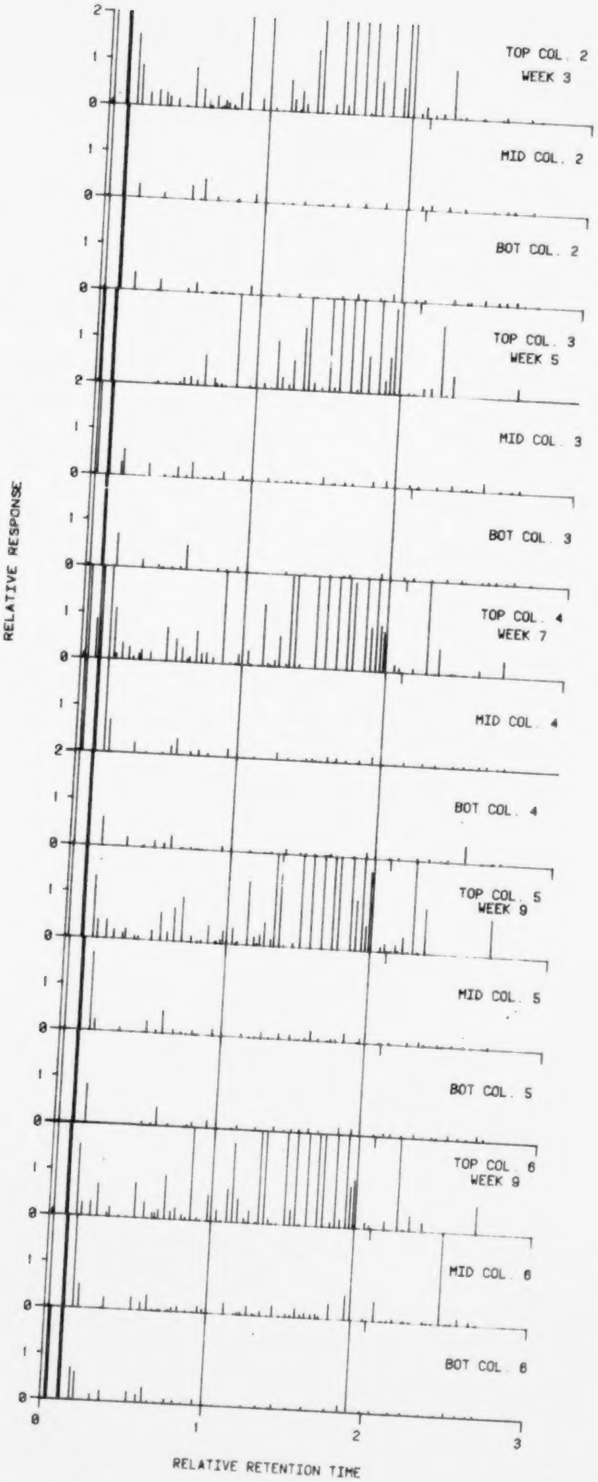

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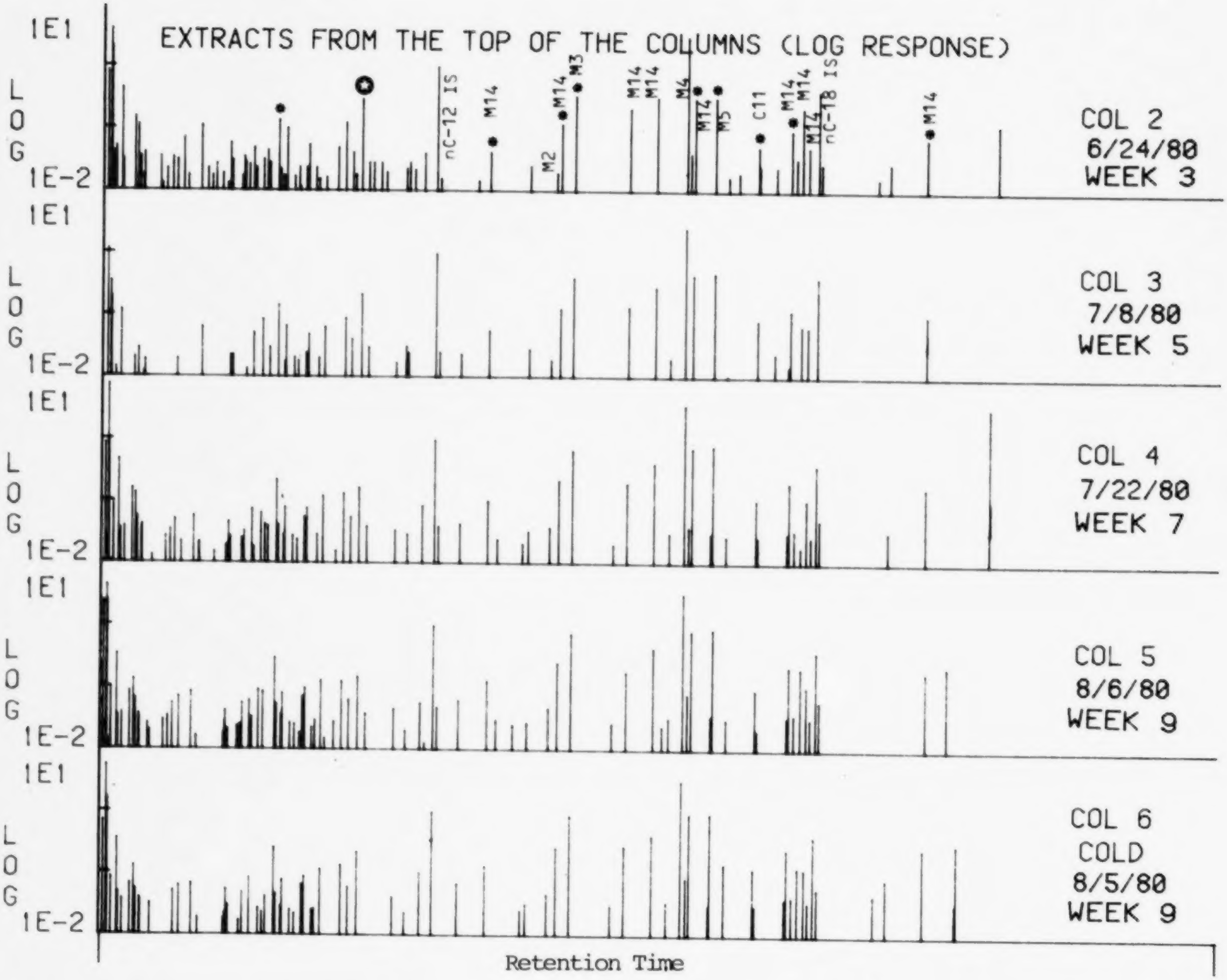

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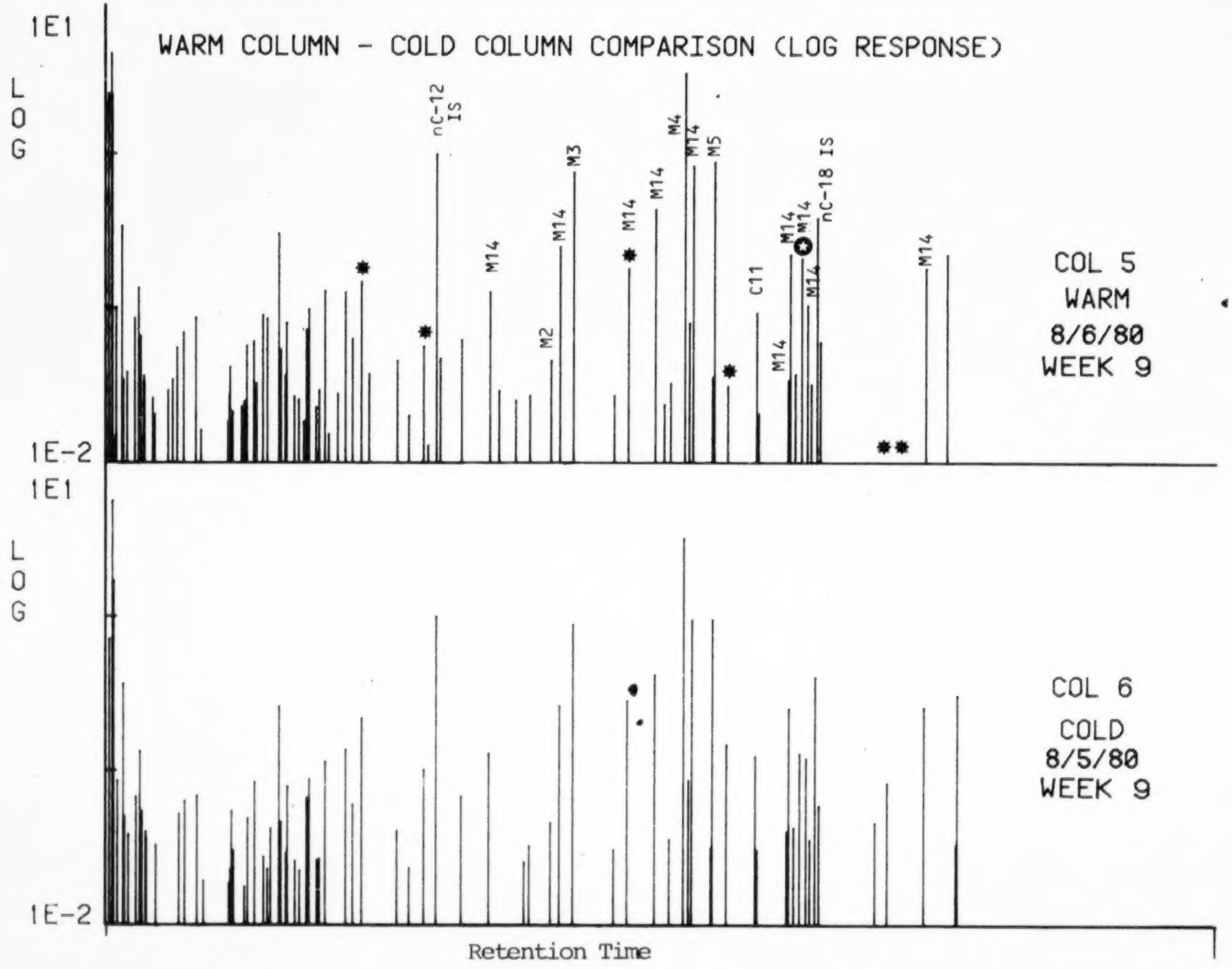

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